

X-RAY STRUCTURE ANALYSIS OF Cu COMPLEXES

By

RAGHAVENDRA TEWARI

PHY

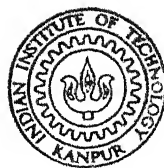
1973

D

TEW

RAY

T14
Phy/1973/D
T31X



DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

OCTOBER, 1973

X-RAY STRUCTURE ANALYSIS OF Cu COMPLEXES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the degree of

DOCTOR OF PHILOSOPHY

by

RAGHAVENDRA TEWARI

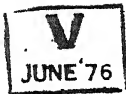
to the

Department of Physics

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

(INDIA)

OCTOBER 1973



PHY-1973-D-TEW-X-RAY

U. T. L. PUR
CENTRAL LIBRARY

Acc. No. A 45561

FEB 1976

dedicated to Sushma, Asha and Ramoo

ACKNOWLEDGEMENT

It gives me great pleasure to express my appreciation and gratitude to Dr. R.C. Srivastava, whose encouragement and guidance during the course of this research work has been of great value.

I am highly grateful to Dr. A. K. Chakravorty for supplying me with interesting crystals and for many stimulating and encouraging discussions. I wish to thank Dr. J. Mahanty for his active interest in my thesis problem and his kind encouragement throughout the course of this work.

I wish to thank Dr. G.L. Dwivedi for many helpful discussions and suggestions. It is impossible to put into words the invaluable help by my wife Dr. Sushma Tewari at various stages of my thesis work like data collection, data preparation, computation and the compilation of results. My warm and sincere thanks are due to Mr. R.D. Hinduja and Mrs. Asha Hinduja for correcting the manuscript and help in compilation of the Tables.

It has been a delightful experience to have known Mr. S.K. Sehgal and Mrs. Suniti Sehgal, whose kind and hospitable nature made my stay at Kanpur a very pleasant and memorable one.

I am thankful to the staff of the Computer Centre in particular to Mr. R.N. Basu, Mr. S. Kapur and Mr. G.P. Gupta for their co-operation. I also wish to thank Mr. R.D. Tripathi for patient typing of this thesis and Mr. H.K. Panda for cyclostyling it.

VITAE

Born in Allahabad in Dec. 1945, Raghavendra Tewari had his earlier education at R.R. Inter College, Allahabad and C.A.V. Inter College, Allahabad. He subsequently did his B.Sc. and M.Sc. from Allahabad University in 1962 and 1965.

He joined the Indian Institute of Technology, Kanpur in July 1966 as a Research Fellow. He presently holds a faculty position in the Department of Computer Sciences, Aligarh Muslim University, Aligarh.

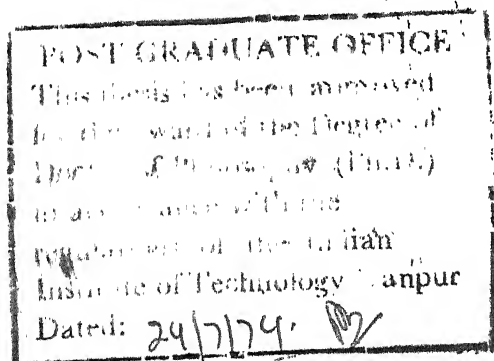
This to certify that the work presented in this thesis
has been carried out by Raghavendra Tewari under my supervision.

R. C. Srivastava

(R.C. Srivastava)
Assistant Professor
Department of Physics

October 1973

Indian Institute of Technology, Kanpur



CONTENTS

	LIST OF TABLES	iv
	LIST OF FIGURES	v
	ABSTRACT	vi
I	INTRODUCTION	1
II	THEORY OF CRYSTAL STRUCTURE ANALYSIS	3
	2.1 Theory of Crystal Structure Analysis	3
	2.2 Corrections to Measured Intensities	3
	a Lorentz and Polarization Corrections	3
	b Absorption Correction	4
	2.3 Atomic Scattering Factor	5
	2.4 Crystal Structure Factor	5
	2.5 Fourier Synthesis	6
	2.6 Phase Problem	8
	2.7 Patterson Synthesis	9
	2.8 Heavy Atom Method	10
	2.9 Test for Correctness of Structure	11
	2.10 Temperature Factor	11
	2.11 Difference Fourier Synthesis	12
	2.12 Least Square Refinement	14
III	THE CRYSTAL STRUCTURE OF Bis(H-PYRROLE-2-ALDIMINE)Cu II	18
	3.1 Experimental	18
	3.2 Structure Determination	22
	3.3 Discussion	32

IV	CRYSTAL STRUCTURE OF $\text{Cu}(\text{Sal})(\text{SalNMe}_2)$	48
4.1	Experimental	48
4.2	Crystal Structure Determination	51
4.3	Refinement	53
4.4	Discussion	54
	APPENDIX I	86
	APPENDIX II	88
	GENERAL REFERENCES	89
	REFERENCES	90

LIST OF TABLES

3.1	Crystal Data Bis(H-pyrrole-2-alimine)Cu II	20
3.2a	Atomic Positions and Their Standard Deviation ($\times 10^4$)	30
3.2b	Anisotropic Temperature Parameters and Their Standard Deviation ($\times 10^4$)	31
3.3	Bond Lengths and Bond Angles and Their Standard Deviation	33
3.4	Deviations of the Atoms From the Best Least Square Plane Eqn.(3.1)	36
3.5	Observed and Calculated Structure Factors	40
4.1	Crystal Data Cu(Sal)(SalNMe ₂)	49
4.2a	Position Parameter Table	55
4.2b	Thermal Parameters $\times 10^5$	56
4.3a	Table Showing the Bond Lengths in Å ($\sigma \times 10^2$)	57
4.3b	Table of Bond Angles in Degrees ($\sigma \times 10$)	58
4.4	Best Plane Equations and Deviations	65
4.5	Calculated and Observed Structure Factors for Cu(Sal)(SalNMe ₂)	68b

LIST OF FIGURES

3.1	Symmetry Elements for Space Group $P2_1/c$	23
3.2	Wilson Plot for Bis(H-pyrrole-2-aldimine)Cu II	25
3.3a	Electron Density Contours of $Y=0$ in Bis(H-pyrrole-2-aldimine)Cu II	28
3.3b	Electron Density Contours at $Y=\frac{1}{4}$ in Bis(H-pyrrole-2-aldimine)Cu II	29
3.4	X-Z Projection of the Molecule Showing Thermal Ellipsoids	34
3.5	Bond Lengths and Angles for Bis(H-pyrrole-2-aldimine)Cu II	35
3.6	X-Z Projection of Bis(H-pyrrole-2-aldimine)Cu II Showing Packing in a Unit Cell	38
4.1	X-Y Projection of the Molecule Showing Thermal Ellipsoids	59
4.2a	X-Y Projection of the Molecule Showing the Bond-Lengths in Å	60
4.2b	X-Y Projection of the Molecule Showing Bond-Angles in Degrees	61
4.3	X-Y Projection of the Square Pyramid Co-ordination	62
4.4	X-Y Projection of the Molecule Showing the Packing	68a

ABSTRACT

Thesis by : Raghavendra Tewari
Department : Physics
Thesis Title : X-Ray Structure Analysis of
Cu Complexes
Programme : Ph.D.
Thesis Supervisor : Dr. R.C. Srivastava

The thesis contains four chapters and two appendices. First chapter introduces the importance of X-Ray crystal structure analysis and discusses the salient features of two Cu complexes whose crystal structure determination has been undertaken. Chapter 2 gives a brief summary of the theory of crystal structure analysis.

Chapter 3 deals with the crystal structure analysis and discussion of the compound Bis(H-pyrrole-2-alimine)Cu II. The main feature of this structure is that the Cu^{++} ion is co-ordinated with four nitrogens in a square planar arrangement. The molecule is planar, the maximum deviation from the plane is 0.06 \AA . The final value of the reliability index R over 552 observed reflections is 0.061.

Chapter 4 contains the crystal structure analysis and discussion of the compound $\text{Cu}(\text{Sal})(\text{SalNMe}_2)$. This structure has been refined to a final R value of 11.0% over 1344 observed reflections. In this compound

Cu is pentacoordinated with three oxygens and two nitrogens in the form of a distorted square pyramid around Cu. Two nitrogens and two oxygens form the basal plane while one oxygen is at the apex.

Appendices I and II describe two computer programs written for IBM 7044 and used in this work.

CHAPTER I

INTRODUCTION

The wave-length of X-Rays is of the same order as the interatomic distances in a crystal; X-Ray diffraction experiments therefore in principle can give information about the position of the constituent atoms of a crystal with respect to a co-ordinate system and hence the bond-lengths, bond-angles and the geometry of the molecule. X-Ray methods also yield information regarding the thermal vibration of atoms about their mean position.

The crystal structure analysis of two Cu complexes was undertaken with a view to learn more about the co-ordination geometry of Cu. The first structure presented in this thesis is that of Bis-(H-pyrrole-2-alimine) cu II. Besides the co-ordination geometry of Cu the pyrrole-2-alimine chelates are of interest because they have structural features common to some compounds of biological importance e.g. porphyrines. The main structural feature of this complex is that the two nitrogens of each ligand are co-ordinated with Cu^{++} in a square planar arrangement.

The second structure presented in this thesis is that of $\text{Cu}(\text{Sal})(\text{Sal}-\text{NMe}_2)$. It was established⁽¹⁾ that Cu, in this compound is penta co-ordinated with two oxygens of one ligand and with two nitrogens and one oxygen of the other ligand. The Cu co-ordination could either be a trigonal bipyramidal or square pyramidal. It has been found from the crystal structure analysis of this compound that the five atoms co-ordinated.

that two oxygens and two nitrogens form the basal -plane and an oxygen is at the apex. The copper oxygen distance of the apex oxygen has been found to be significantly larger than the other Cu-oxygen distances.

The second chapter contains a brief summary of the theory of X-Ray structure analysis and refinement. The third chapter deals with the experimental aspects of crystal structure and determination and the discussion of the structure of Bis(-H-pyrrole-2-alimine) cu II. Chapter IV describes the crystal structure analysis and the discussion of the structure of Cu(Sal)(SalNMe₂). Appendix I and Appendix II describe some of the computer programs used.

CHAPTER II

2.1 Theory of Crystal Structure Analysis

When a beam of X-Rays is incident on a single crystal, it gets diffracted. The intensity of diffracted X-Rays in different directions depends on the orientation of the crystal with respect to the incident beam. A measurement of intensities and positions of these diffraction maxima forms the basic data for X-ray structure analysis work. Their positions are used for identifying them with crystal planes and for assigning hkl indices and also for the determination of the unit cell dimensions of the crystal. The systematic absences of a certain class of diffraction maxima yield information about the space group symmetry of the crystal.

2.2 Corrections to the Measured Intensities

The observed intensities of diffraction maxima are however, affected by some geometrical and physical factors, for which they must be corrected before they are used for interpreting diffraction experiments. These corrections are briefly discussed in the following sections.

2.2(a) Lorentz and Polarization Corrections

Since the time required by a reciprocal lattice point to pass through the sphere of reflection, depends on its position in reciprocal space and the direction in which it approaches the sphere, a correction depending purely on the geometry of observation has to be applied. This is known as Lorentz correction and for the present (diffractometer with single crystal orienter) case, it is $\frac{1}{2\sin 2\theta}$, where θ is the Bragg

angle of the reflection. Another correction, known as the polarization correction has to be applied because the incident X-Ray beam is unpolarized. The correction is $\frac{1}{2}(1 + \cos^2 2\theta)$. Thus the corrected intensity $I(hk1)$ can be written as

$$I(hk1) = I_o(hk1) \frac{2 \sin^2 \theta}{(1 + \cos^2 2\theta)} \quad \dots (2.1)$$

where $I_o(hk1)$ is the observed intensity of the reflection $hk1$.

2.2(b) Absorption Correction

Since the path travelled by the incident and the diffracted rays inside the crystal for different reflections is different, their intensities are attenuated differently. An accurate estimate of absorption correction for each reflection for any general geometry of the crystal is an extremely difficult and time consuming task. However, if the crystal is of a regular shape or is ground to a regular shape and an accurate measurement of the dimensions is done, a realistic absorption correction⁽²⁾ can be applied. In crystal of low absorption coefficients and not too regular a shape the corrections due to absorption may be small (of the order of the inaccuracy involved in intensity measurement) and may be neglected. Moreover, the absorption error affects the temperature factors only, leaving the position parameters unaffected⁽³⁾. Hence, in crystal structures where interpretation of temperature factor is not of vital importance the absorption correction may be neglected unless it is much too large.

2.3 Atomic Scattering Factor

If an electron is located in the path of an X-Ray beam, it is forced into oscillations by the electromagnetic field of the X-rays impinging upon it. Due to this acceleration, the electron in turn becomes a source of radiation, and in this way the electron is said to scatter the impinging radiation. Each chemical atom has a specific number of electrons associated with it in space, the specific form of the distribution of electrons about each atom being known from the atomic structure theory. If the amplitude of the wavelet scattered by an electron is taken as the unit amplitude, then the amplitude scattered by an atom (here after referred as atomic scattering factor) can be written as the sum of unit amplitudes of the wavelets, properly phased, which are scattered by the individual electrons in the atom. Thus the scattering factor 'f' of an atom is expressed in terms of the scattering power of a single free electron. The maximum value of the atomic scattering factor of an atom is therefore equal to z, its atomic number. This value occurs at $\frac{\sin \Theta}{\lambda} = 0$. If the electrons of an atom were concentrated at a single point, there would be no destructive interference between the wavelets scattered by them and there would be no variation of f with $\frac{\sin \Theta}{\lambda}$. But since the electrons of actual atoms are distributed over the volume of the atom, destructive interference sets in, and larger the volume of an atom, the greater is the fall-off of f with $\frac{\sin \Theta}{\lambda}$.

2.4 Crystal Structure Factor

Crystal structure factor F_{hkl} is defined as the sum of the wavelets scattered due to each atom in the unit cell, in the direction of the Bragg

reflection from the plane hkl . Thus it can be written as

$$F_{hkl} = f_1 e^{2\pi i(hx_1 + ky_1 + lz_1)} + f_2 e^{2\pi i(hx_2 + ky_2 + lz_2)} + \dots \\ \dots + f_j e^{2\pi i(hx_j + ky_j + lz_j)} \dots (2.2)$$

$$= \sum_{j=1}^J f_j e^{2\pi i(hx_j + ky_j + lz_j)} \dots (2.3)$$

Where f_j is the atomic scattering factor of the j th atom located at x_j , y_j and z_j and J is the total number of atoms in the unit cell.

The equation 2.3 can also be written as

$$F_{hkl} = |F_{hkl}| \cos \phi_j + i |F_{hkl}| \sin \phi_j \quad (2.4)$$

where $|F_{hkl}|$ is the absolute value of the structure amplitude, and

$$\phi_j = 2\pi(hx_j + ky_j + lz_j) \quad \dots (2.5)$$

ϕ_j 's are called the phase angle of the structure amplitude.

These can be computed as

$$\phi_j = \tan^{-1} \left[\frac{\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)}{\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)} \right] \quad \dots (2.6)$$

2.5 Fourier Synthesis

Instead of assuming discrete atoms located at x_j , y_j and z_j it may be assumed that the crystal is composed of an electron density

$\rho(x_j, y_j, z_j)$ which varies continuously over the volume of the unit cell, then the structure factor can be expressed as

$$F_{hkl} = \int_0^V \rho(xyz) e^{2\pi i(hx + ky + lz)} dV \quad \dots(2.7)$$

where dV is an infinitesimal volume element and V is the unit cell volume. Since the electron density $\rho(x, y, z)$ in a crystal is a periodic function in three dimension, it can be represented by a three dimensional fourier series

$$\rho(x, y, z) = \sum_h \sum_k \sum_l^{+\infty} K_{hkl} e^{-2\pi i(\frac{hX}{a} + \frac{kY}{b} + \frac{lZ}{c})} \quad \dots(2.8)$$

Where K_{hkl} are the fourier coefficients. It can be shown that the fourier coefficients of this expansion eqn. (2.8) are (F_{hkl}/V) .

Thus (2.8) can be written as

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l^{+\infty} F_{hkl} e^{-2\pi i(hx + ky + lz)} \quad \dots(2.9)$$

Thus a three dimensional plot of ρ (xyz) will show peaks at those (x,y,z) positions where the atoms are situated.

2.6 Phase Problem

Equation (2.4) can be written as

$$F_{hkl} = |F_{hkl}| e^{2\pi i \frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z} \quad \dots(2.10)$$

Thus crystal structure factors F_{hkl} are characterized by both, a magnitude and a phase. The magnitude is known experimentally because

$$I_{hkl} = |F_{hkl}|^2 \quad \dots(2.11)$$

But the experiments do not give us any direct information about the phase and hence the experimental data is not sufficient for performing the fourier synthesis. At the first sight therefore, it appears that crystal structures are indeterminate because of the lack of the information about phases of structure factors. However, if there could be some way of knowing these phases, then it would be a routine to find the arrangement of atoms by doing just one fourier synthesis. The peaks in a electron density plot obtained from fourier synthesis give the position of the atoms.

In the absence of any direct information about phase, the crystal structures are solved by eliciting the information regarding phases in an indirect way. There are many methods⁽⁴⁾ for obtaining the phases indirectly and one chooses a particular procedure depending on the kind of structure one has to solve. We have used the Heavy Atom

method with Patterson synthesis. Both of these are discussed in the following sections.

2.7 Patterson Synthesis

Patterson⁽⁵⁾ synthesis is a fourier synthesis with the fourier coefficients as $\frac{|F_{hkl}|^2}{V}$ or I_{hkl} instead of F_{hkl} in equation (2.9).

$$P(u,v,w) = \frac{1}{V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} I_{hkl} e^{2\pi i(hu + kv + lw)} \quad \dots(2.12)$$

Where $P(u,v,w)$ is known as the patterson's function and is defined as

$$P(u,v,w) = \iiint_0^1 \rho(xyz) \rho(x+u,y+v,z+w) dx dy dz \quad \dots(2.13)$$

This is a self convolution of electron density. The peaks in $P(u,v,w)$ correspond to the interatomic vectors of the atoms in the unit cell, and the magnitude of these maxima would be $f_i f_j$ for the peak due to i th and j th atom. The parameters u , v and w correspond to $(x_i - x_j)$, $(y_i - y_j)$ and $(z_i - z_j)$ respectively. If there are N atoms in a unit cell, there will be $(N^2 - N)$ maxima. Therefore, the number of peaks in a Patterson Synthesis will in general be very large and many peaks would overlap. However, if there are one or more heavy atoms present, the heavy atom-heavy atom peaks would be very large in magnitude as compared to the others. In many such cases it is possible to get the position of heavy

atoms by Patterson synthesis and a knowledge of the symmetry of the crystal.

2.8 Heavy Atom Method

The basic assumption of heavy atom method is that the phases of all the reflections are predominately determined by the heavy atom only. As a rough guide, for successful use of the method the sum of the squares of the atomic numbers of heavy atoms and the light atoms should be approximately equal. Sim⁽⁶⁾ defines a quantity

$$r = \frac{f_H^2}{\sum f_L^2} \quad \dots(2.14)$$

Where f_H and f_L are the atomic scattering factors of heavy and light atoms respectively. For the values of r approximately equal to one, the proportion of correct phases is large. However, crystal structures with considerably less than one have also been solved.

Once the position of the heavy atom is known by Patterson synthesis or other means, a fourier synthesis (henceforth referred to as Fo-synthesis) is done with the observed structure amplitudes as the fourier coefficients and the phases due to the heavy atom only. This Fo-synthesis is expected to show well defined maxima for the heavy atom and in addition some peaks due to light atoms also, because it contains information about all the atoms in the unit cell. Some light atoms which are located in this synthesis are included in the calculation for phases in the next Fo-synthesis and thus successive Fo-synthesis reveal the whole structure.

2.9 Test for Correctness of a Structure

The correctness of a structure is determined by comparing the observed structure factors with the calculated F_{hkl} on the basis of proposed arrangement of atoms. If the two structures are identical in every way, they will produce identical set of diffraction maxima. Small deviations between them can be attributed to the errors in the measurement of intensities. Several factors for assessing the discrepancy have been proposed in the literature⁽⁷⁾. We have used the factor R known as the reliability index (henceforth referred to as R only) as a measure of the correctness of the structure. R is defined as

$$R = \frac{\sum_n | |F_{hkl}^o| - |F_{hkl}^c| |}{\sum_n |F_{hkl}^o|} \quad \dots\dots(2.15)$$

where n is the total number of observations used.

2.10 Temperature Factor

Atoms in a crystal undergo thermal vibration about their mean position at all temperatures. This causes the effective f (atomic scattering factor) to fall off more rapidly with $(\frac{\sin \theta}{\lambda})$ than for the same atom at rest. Each atom undergoes a motion such that its electron density is smeared over a volume, usually regarded as a triaxial ellipsoid in a general case. Every non-equivalent atom not only corresponds to a different ellipsoid but also the ellipsoids are oriented differently.

Obviously, consideration of such a complex motion is extremely difficult and not very meaningful in the earlier stages of the structure determination when the model is crude. So, in the initial stages, all the atoms are assumed to have the same thermal motion and an overall isotropic temperature correction (B_o) defined in the following manner is applied.

$$f = f_o e^{-(B_o \sin^2 \Theta) / \lambda^2} \quad \dots(2.16)$$

where f_o is the scattering factor of the static atom. As the structure gets refined, every non-equivalent atom is assumed to have a different isotropic thermal motion, making the electron density of each atom to smear into a sphere of different size. This leads to individual atom isotropic temperature factor (B_j) defined as

$$f_j = f_{oj} e^{-(B_j \sin^2 \Theta) / \lambda^2} \quad \dots(2.17)$$

When the structure is in the final stages, the atomic thermal motion can be approximated by a triaxial ellipsoid, which is different for each non-equivalent atom. This leads to a six component anisotropic temperature factor defined in the following manner.

$$f_j = f_{oj} e^{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)} \quad \dots(2.18)$$

2.11 Difference Fourier Synthesis

Difference fourier synthesis^(8,9,10) is a single fourier synthesis using $(F_{hkl}^o - F_{hkl}^c)$ as the fourier coefficients.

$$(\rho_o - \rho_c) = \frac{1}{V} \sum_h \sum_k \sum_l (F_{hkl}^o - F_{hkl}^c) e^{-2\pi i(hx+ky+lz)} \dots (2.19)$$

Difference fourier synthesis is used for refinement of the structure because of the following interesting properties.

It does not suffer from the series termination effects which are present in F^o -synthesis. Since difference synthesis is equivalent to a point by point subtraction of a F_{hkl}^c -synthesis from a F_{hkl}^o -synthesis, the spurious peaks due to series termination get subtracted out. This happens because these spurious peaks due to series termination will be in the same position in F_{hkl}^o -synthesis as in F_{hkl}^c -synthesis. Furthermore, if an atom has been correctly placed and the temperature factor is also right, difference synthesis will show a flat general background at that position. However, if an atom has been placed incorrectly, difference synthesis shows postulated position as a hole (negative electron density) and the correct position as a peak. If these positions are not far apart then one can calculate the shift needed to reach the correct atomic position from the slope of the electron density between the postulated and correct position.

The atoms not included in F_c -calculation will show up as peaks in the difference fourier synthesis. Thus it also helps in locating the unresolved atoms in F_o -synthesis. Thermal parameters can also be

refined by difference synthesis because an under or over-estimation of isotropic thermal parameters will show up as positive or negative remanant electron density respectively at the assigned atomic position in the difference synthesis.

If there is anisotropic thermal motion, the observed electron density distribution at the peak appears to be drawn out in the direction of maximum vibration and narrowed in a direction rightangles to it. This thermal anisotropy will show up clearly in difference synthesis. Thus from the shape of electron density in difference synthesis it is possible to compute anisotropic temperature factors^(10,11,12).

2.12 Least Square Refinement

F_{hkl}^c (calculated structure factor) is a function of the scale constant, position parameters and temperature factors of all the atoms in the unit-cell. Since the observed structure factors F_{hkl}^o are subject to the errors of observation, the final stage in the refinement of a crystal structure should involve varying all the above mentioned parameters by a small amount to obtain a better agreement between the calculated structure factors F_{hkl}^c and the observed structure factors F_{hkl}^o . This is done by the method of Least squares. The quantity minimized is

$$\mathcal{L} = \sum_{hkl} w_{hkl} (|F_{hkl}^o| - |kF_{hkl}^c|)^2 \quad \dots (2.20)$$

where \sum_{hkl} indicates a sum over all the observed reflections, w_{hkl} is the weight of each reflection hkl . Since F_{hkl}^c is a function of n

parameters $p_1, p_2, p_3 \dots p_n$ which may be any of the scale, position or the thermal parameters, the first derivative of \mathcal{L} with respect to each of these parameters should be equated to zero for a minimum.

$$F_{hkl}^c = F_{hkl}^c(p_1, p_2, p_3 \dots p_n) \quad \dots(2.21)$$

Equating the first derivative of \mathcal{L} defined through (2.20) to zero leads to n normal equations of the type.

$$\sum_{hkl} w_{hkl} (|F_{hkl}^c| - |kF_{hkl}^c(p_1, \dots, p_n)|) \frac{|kF_{hkl}^c(p_1, \dots, p_n)|}{\partial p_j} = 0 \quad \dots(2.22)$$

where $j = 1, \dots, n$

$|F_{hkl}^c|$ can be expanded in a Taylor series of the following form with the second and higher orders neglected.

$$|kF_{hkl}^c(p_1 \dots p_n)| = |kF_{hkl}^c(a_1 \dots a_n)| + \frac{\partial |kF_{hkl}^c|}{\partial p_1} \Delta p_1 + \dots + \frac{\partial |kF_{hkl}^c|}{\partial p_n} \Delta p_n \quad \dots(2.23)$$

Where $a_1 \dots a_n$ are the initial values of the parameters and $\Delta p_j = p_j - a_j$. Now, substituting equation (2.23) in equation (2.22) and rearranging the terms we get the following set of n normal equations.

$$\sum_{hkl} w_r \frac{\partial |kF_r^c|}{\partial p_n} \times \frac{\partial |kF_r^c|}{\partial p_1} \Delta p_1 + \dots +$$

$$\sum_{hkl} w_r \left(\frac{\partial |kF_r^c|}{\partial p_n} \right)^2 \Delta p_n = \sum_{hkl} w_r \Delta F_r \frac{\partial |kF_r^c|}{\partial p_n} \dots (2.24)$$

$$r = 1, 2, \dots, n$$

where K is the scale constant, F_r^c is the value of F_{hkl}^c for the r th observation and F_r is the value of $|F_{hkl}^o - KF_{hkl}^c|$ which plays a role of the known observable quantity for the r th observation. We can write the above n normal equations in a matrix form if we write

$$C_{ij} = \sum_{hkl} w_r \frac{\partial |kF_r^c|}{\partial p_i} \times \frac{\partial |kF_r^c|}{\partial p_j}$$

$$x_j = \Delta p_j$$

and

$$V_j = \sum_{hkl} w_r (\Delta F_r) \frac{\partial |kF_r^c|}{\partial p_j} \dots (2.25)$$

The above n normal equations can then be written in a matrix form

$$\text{as } \begin{bmatrix} C_{11} & C_{12} & C_{1n} \\ C_{21} & C_{22} & C_{2n} \\ - & - & - \\ - & - & - \\ C_{n1} & C_{n2} & C_{nn} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ - \\ - \\ X_n \end{bmatrix} = \begin{bmatrix} V_1 \\ V_2 \\ - \\ - \\ V_n \end{bmatrix} \quad (2.26)$$

or in a more compact form as

$$\underline{C} \cdot \underline{X} = \underline{V} \quad (2.27)$$

The equations (2.26) can be solved for X_j if an inverse of the matrix C exists. Thus

$$\underline{X} = \underline{C}^{-1} \cdot \underline{V} \quad \dots(2.28)$$

and one can get the value of X_j which is nothing but Δp_j or $(p_j - a_j)$. These Δp_j 's can be combined with the initial values of the parameters i.e., a_j 's to give a better set of parameters. This process may be repeated until successive cycles produce no appreciable change in the values of the parameters. When the calculated shifts in parameters become small as compared to the standard deviation of the parameters further cycles of refinement may be stopped.

The general equation for calculating the standard deviation⁽¹³⁾

σ_{p_j} for any parameter p_j

$$\sigma_{p_j} = \sqrt{C_{jj}^{-1} \left(\sum_{hkl} w_r \Delta F_r^2 \right) / (N-n)} \quad \dots(2.29)$$

where N is the total number of observations over which the summation \sum_{hkl} is carried out, n is the number of parameters varied and C_{jj}^{-1} is the j th diagonal element of the inverse matrix C^{-1} .

CHAPTER III

THE CRYSTAL STRUCTURE OF BIS(H-PYRROLE-2-ALDIMINE)Cu II

3.1 Experimental

The crystals of Bis(H-pyrrole-2-alimine)Cu II were grown by slow evaporation of its solution in AR grade toluene. The crystals come out as hexagonal plates of deep purple brown colour. Suitable crystals of approximately 0.20 x 0.15 x 0.15 mm were chosen for X-Ray studies.

Preliminary studies of the crystal were done photographically with the help of rotation and Weissenberg methods.

The crystals were found to belong to monoclinic class. A crystal was mounted along b axis (unique) and rotation, zero, first and second layer Weissenberg photographs were recorded. Filtered $\text{CuK}\alpha$ radiation was used. Weissenberg photographs showed the following systematic absences; $h0l$ reflections absent when $l = 2n + 1$ and $0k0$ reflections absent when $k = 2n + 1$. These systematic absences fix the space group uniquely as P_{21}/c .

The crystal was later on transferred to General Electric XRD-6 diffractometer equipped with a quarter circle goniostat. The lattice constants a, b, c and β were accurately determined by using the high order axial reflections. The reflections 400 , 500 , 600 , 700 , 800 and 900 were used for the determination of a, 020 , 040 and 060 for the determination of b and the reflections 004 , 006 , 008 and 0010 for the determination of c. A slow scan in 2θ of the above reflections was made and mean 2θ corresponding to half the peak intensity was taken as the 2θ for calculations

of lattice parameter after correcting it for the zero error in 2θ scale.

The angle β^* was determined by directly noting down the angle between a^* and c^* axes by rotating the ϕ circle of the goniostat. The lattice parameters thus determined are listed in table 3.1.

Density of the crystals was measured by the floatation method. The two liquids employed were distilled water and a saturated solution of zinc chloride. The calculated and measured densities are listed in Table 3.1.

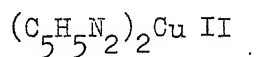
Once the lattice parameters were known, the ψ , χ and 2θ settings of the goniostat for all the hkl and $\bar{h}kl$ reflections within the $CuK\alpha$ sphere of reflection were calculated using a computer program⁽¹⁴⁾ written for IBM 7044 computer. The reflections were divided in four different shells of 2θ viz., 0° - 60° , 60° - 80° , 80° - 100° and 100° - 120° , and reflections in each shell were sorted on 2θ , χ and ψ angles respectively for ease in data collection. Reflections which were found systematically absent on the Weissenberg photographs were again checked on the diffractometer and the space group assignment of P_{21}/c was further confirmed. These results agree with those of Stakleberg⁽¹⁵⁾.

Three dimensional intensity data were collected using the stationary crystal stationary counter technique. A random check of the width of reflections was made and it was found that the peak width was always less than 2° . The intensity of a reflection was counted at the 2θ value corresponding to the peak intensity for ten seconds and then the 2θ angle was offset on the high 2θ side by one degree and the back-ground on the high 2θ side was also counted for ten seconds. The background on low 2θ side

TABLE 3.1

Crystal Data

Bis(H-pyrrole-2-alimine)Cu II



Crystal Class : - Monoclinic

Space group : - P_{21}/c

$$\underline{a} = 9.845 \pm .002 \text{ \AA}$$

$$\underline{b} = 5.562 \pm 0.003 \text{ \AA}$$

$$\underline{c} = 9.604 \pm .003 \text{ \AA}$$

$$\beta = 103.07 \pm 0.01^\circ$$

$$\text{Measured Density} = 1.59 \pm 0.02 \text{ gm cm}^{-3}$$

$$\text{Calculated Density} = 1.62 \text{ gm cm}^{-3}$$

$$\text{Number of molecules per unit cell} = 2$$

was also counted in the same way for ten seconds. Filtered $\text{CuK}\alpha$ radiation was used.

Ten reflections of good intensity were picked up covering the whole range of χ, ϕ, ψ from all the reflections and were used as standard reflections. The intensities of these reflections were monitored every twelve hours as a check for mis-alignment or loss in intensity due to irradiation of the crystal or any other fault. There was no significant loss of intensity due to irradiation of the crystal during the course of data collection.

The reflections having intensity more than 20,000 counts per 10 seconds were recorded with additional Ni-absorbers put in front of the counter window. The filter factors for these absorbers were determined by choosing a few strong reflections out of those which were recorded without the additional absorbers. They were again recorded with absorbers and the ratio of the counts gave the filter factor for the absorber. There were only ten reflections for which additional absorbers were needed.

It was found that beyond 2θ angle of 100° , more than two thirds of reflections had intensity almost equal to the background. Hence, intensity measurements beyond this 2θ angle were not made. The intensity data for a total of 730 reflections were recorded. The reflections, whose intensity differed from the background by less than one standard deviation of the background were classified as unobserved. There were 178 such unobserved reflections.

The background correction was obtained by taking the arithmetic mean of the background on high and low 2θ side. This was subtracted from the total counts corresponding to a reflection and the resulting number of counts were taken as observed integrated reflection. Appropriate Lorentz and Polarization corrections were also made to the intensities. These corrections were applied through a computer program⁽¹⁶⁾ written for IBM 7044 computer. Besides correcting the intensities for Lorentz and Polarization factors and the background, this program also calculates $|F|$ and sorts the reflections on the indices h, k and l in the desired sequence.

In order to assess the correction needed because of absorption, the intensities of $0,2,0$ ($2\theta = 32.0^\circ$), $0,4,0$ ($2\theta = 67.4^\circ$) and $0,6,0$ ($2\theta = 112.6^\circ$) reflections which occur at $\chi = 90^\circ$ was examined for 360° rotation of the ϕ circle of the goniostat. It was found that the maximum variation in intensity of any of these reflections was less than 10%. The absorption correction was thus small and was therefore neglected.

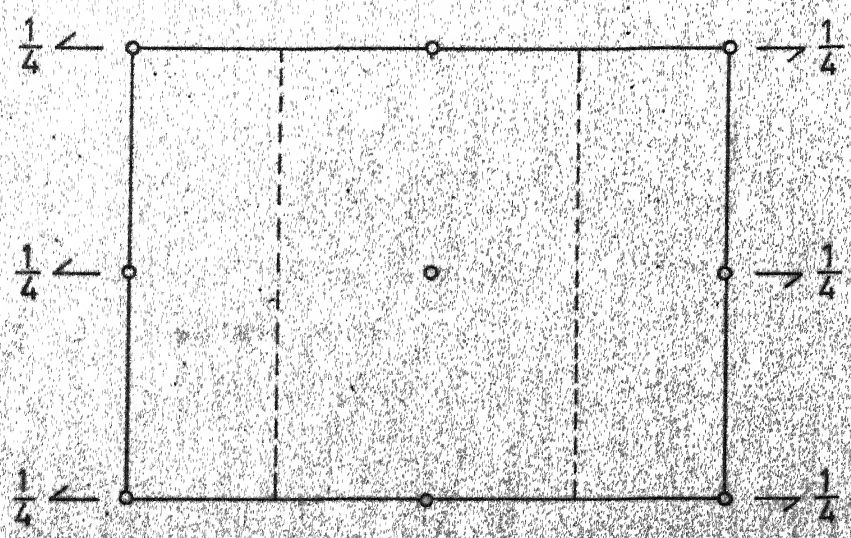
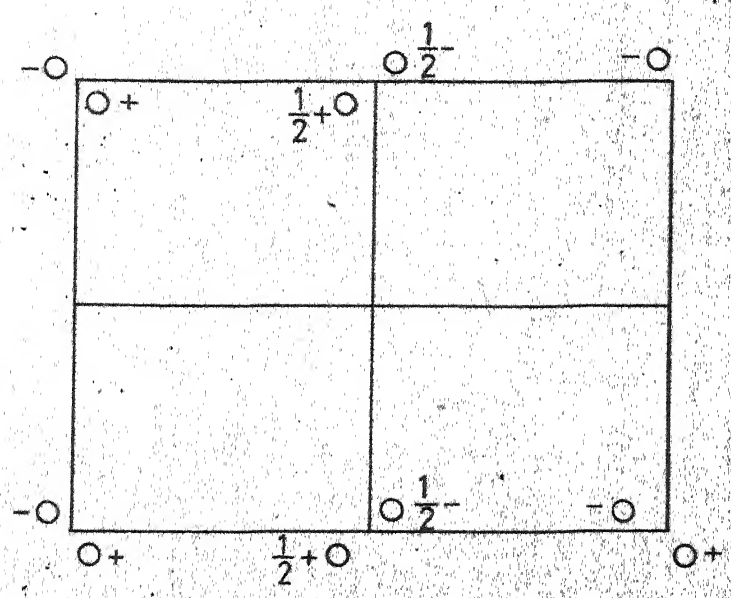
3.2 Structure Determination

Symmetry operations of the space group P_{21}/c are shown in Fig.

3.1. It has four general equivalent positions viz, (x, y, z) , $(x, \frac{1}{2} + y, \frac{1}{2} + z)$; (x, y, \bar{z}) and $(x, \frac{1}{2} - y, \frac{1}{2} - z)$. Since there are only two molecules per unit cell, only half of the molecule will form the asymmetric unit, and two Cu^{++} should occupy one of the sets of twofold centrosymmetric special positions. The set chosen was $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$.

The positions of Cu^{++} thus being fixed by symmetry, a structure factor calculation was done with Cu^{++} at position $(0, 0, 0)$. The weight

No.14 $P2_1/C$
 C_{2h}^5



origin $\bar{1}$ at $\bar{1}$ unique axis b

Fig.3.1 Symmetry elements for space group $P2_1/C$

assigned to this Cu^{++} was 0.5 because only half of Cu^{++} is in the asymmetric unit. An overall temperature factor of 4.8 \AA^2 as determined by the method of Wilson⁽¹⁷⁾, was used. The Wilson plot is shown in Fig. 3.2.

A three dimensional fourier synthesis using the observed structure amplitudes as co-efficients and the phases due to Cu^{++} only showed three outstanding peaks and a few other peaks.

Two out of these three peaks were assigned to carbon atoms and one to nitrogen atom, on the basis of the expected Cu-C and Cu-N distances.

A structure factor calculation was done with half Cu^{++} , one nitrogen and two carbons in the asymmetric unit and the value of R reduced to 0.39. Individual atom isotropic temperature factors were introduced at this stage on the basis of two successive difference fourier ($F_o - F_c$) synthesis. A three dimensional fourier synthesis at this stage based on the phases calculated with the above atoms showed some new peaks and the peaks corresponding to the given atoms showed improvement. Some of these new peaks appeared to correspond to carbon atoms but structure factor calculations by including them one by one with $B = 4.8 \text{ \AA}^2$ (the overall isotropic B) showed that the R was reduced to 0.30 by one of these positions only. This position was then assigned to the third carbon atom. A three dimensional fourier synthesis with the phases due to 0.50 Cu^{++} , one nitrogen, and the above mentioned three carbons in the asymmetric unit revealed the remaining nitrogen and carbon atoms of the molecule. A molecule thus formed looked stereo-chemically reasonable.

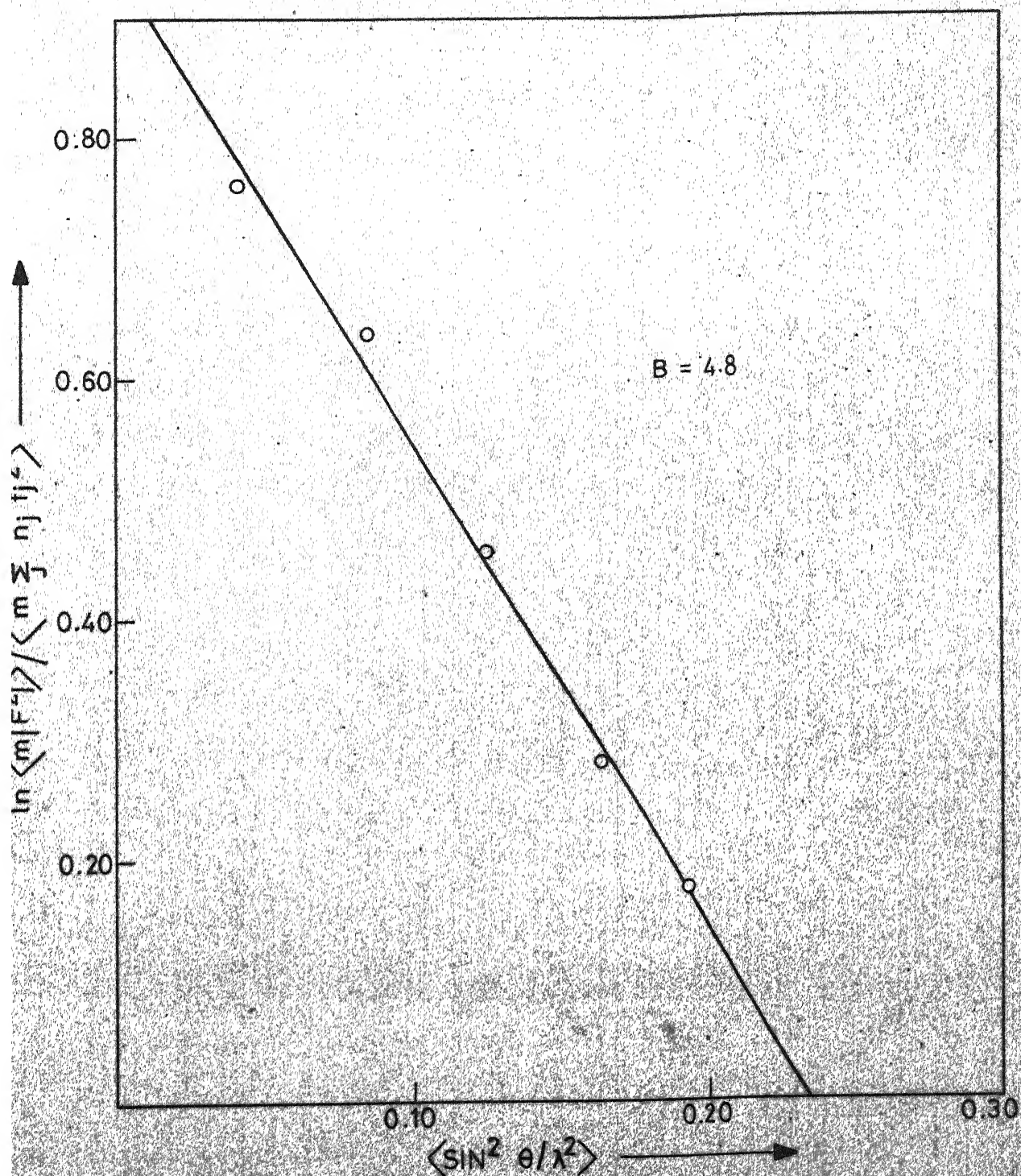


Fig. 3.2 Wilson plot for bis(H-pyrrol-2-alldimine) Cu II.

A structure factor calculation was done by giving all the atoms in the asymmetric unit and $B = 4.8 \text{ \AA}^2$ (the overall isotropic B), the value of R obtained was 0.18. Isotropic temperature factors and the positions of all the atoms were further refined by two successive fourier and difference fourier synthesis. This refinement further decreased the value of R to 0.15.

Position parameters of all the atoms except that of Cu^{++} , isotropic temperature factors of all the atoms and the scale constant were then refined by the full matrix least squares method. The computer program employed for this calculation is an adapted version of Busing, Levy and Martin's⁽¹⁸⁾ program. All the reflections in this refinement were given unit weights. The scattering factor tables for the above calculations were taken from the International table for X-Ray Crystallography⁽¹⁹⁾. The value of R at the end of two cycles of refinement was 0.12.

At this stage the isotropic temperature factors were converted to anisotropic temperature factors of the form

$$\exp \left(- \left\{ h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23} \right\} \right)$$

Three cycles of full matrix least squares refinement was carried out, varying all the parameters except the position parameters of Cu^{++} , which are fixed by symmetry. The value of R at the end of three cycles of refinement reduced to 0.063. The least square refinement was stopped at this stage as the shifts in parameters had reduced to a very small fraction of the standard deviation.

A three dimensional difference fourier synthesis at this stage showed two out of the five hydrogen atoms clearly. The other three hydrogen atoms were assigned calculated positions. These were calculated assuming that the hydrogen atoms were located at a distance of 1.08 \AA on the line bisecting the angle described by the two bonds at the atom to which this hydrogen atom is attached. This calculation was done using the computer program written for IBM 7044 computer.

One cycle of full matrix least square refinement was done including the hydrogen atoms but varying the position, anisotropic temperature parameters and the scale constant of non-hydrogen atoms. The hydrogen atoms were assigned isotropic B of the atoms to which they are attached.

The value of R at the end of one cycle of refinement dropped to 0.061 with observed reflections only and 0.080 with unobserved reflections included. The maximum shifts in the position parameters was 0.25σ whereas the average shift was 0.10σ . Similarly the maximum shift in anisotropic temperature factor parameters was 0.33σ and the average shift was 0.12σ . The least squares refinement was stopped at this point.

A three dimensional fourier synthesis was done at this stage just to provide an additional check on the structure. This is shown in Fig. 3.3(a) and 3.3(b).

The final parameters, their shift in the last cycle of least square refinement and the standard deviations are listed in Table 3.2a and Table 3.2b. The observed and calculated structure factors are tabulated in Table 3.5. Table 3.3 gives the bond lengths, bond angles and their standard deviations.

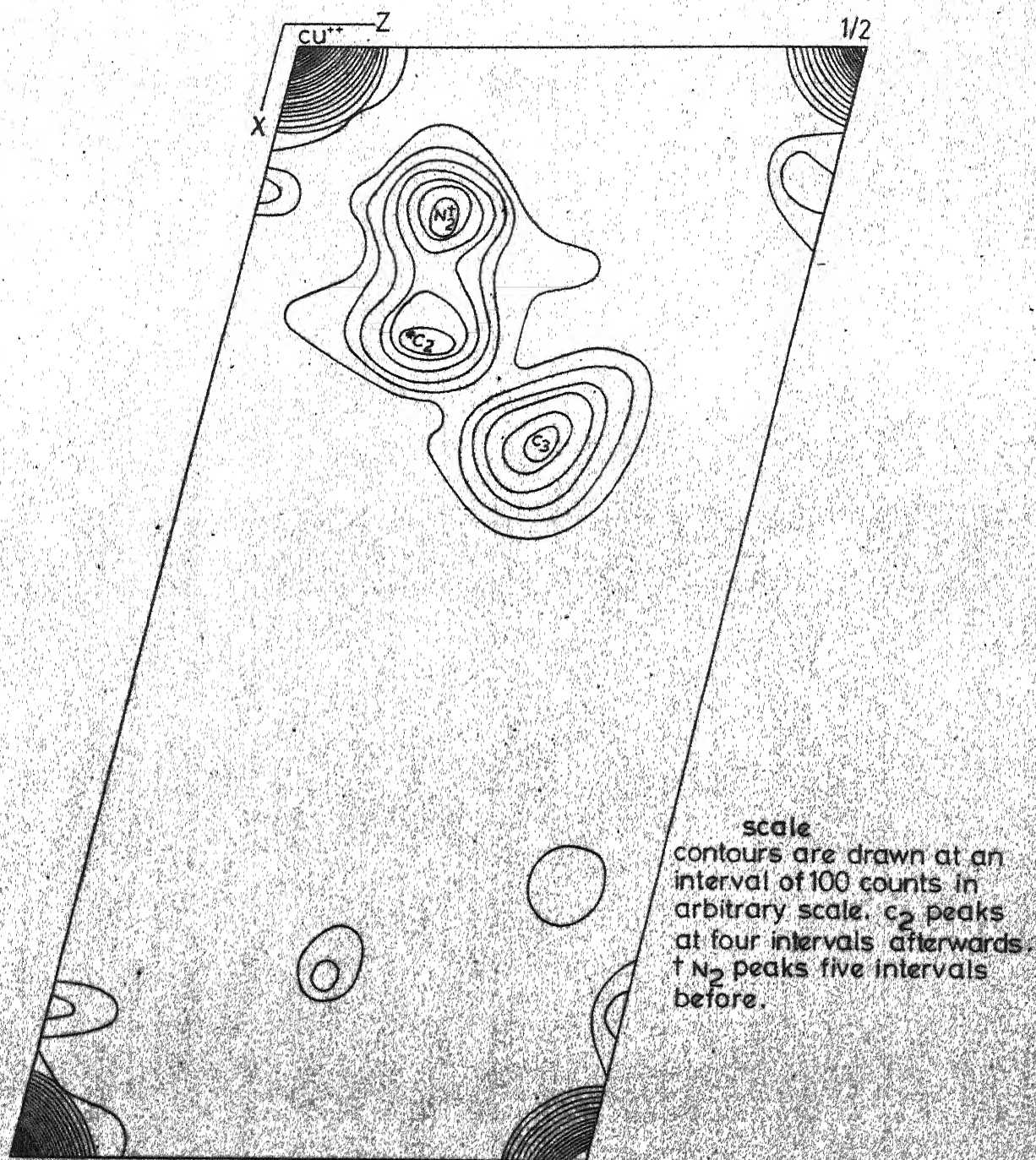


FIG. 3.3a ELECTRON DENSITY CONTOURS OF $Y=O$ IN $Bis(H-PYRROLE$
ALDIMINE) $Cu II$.

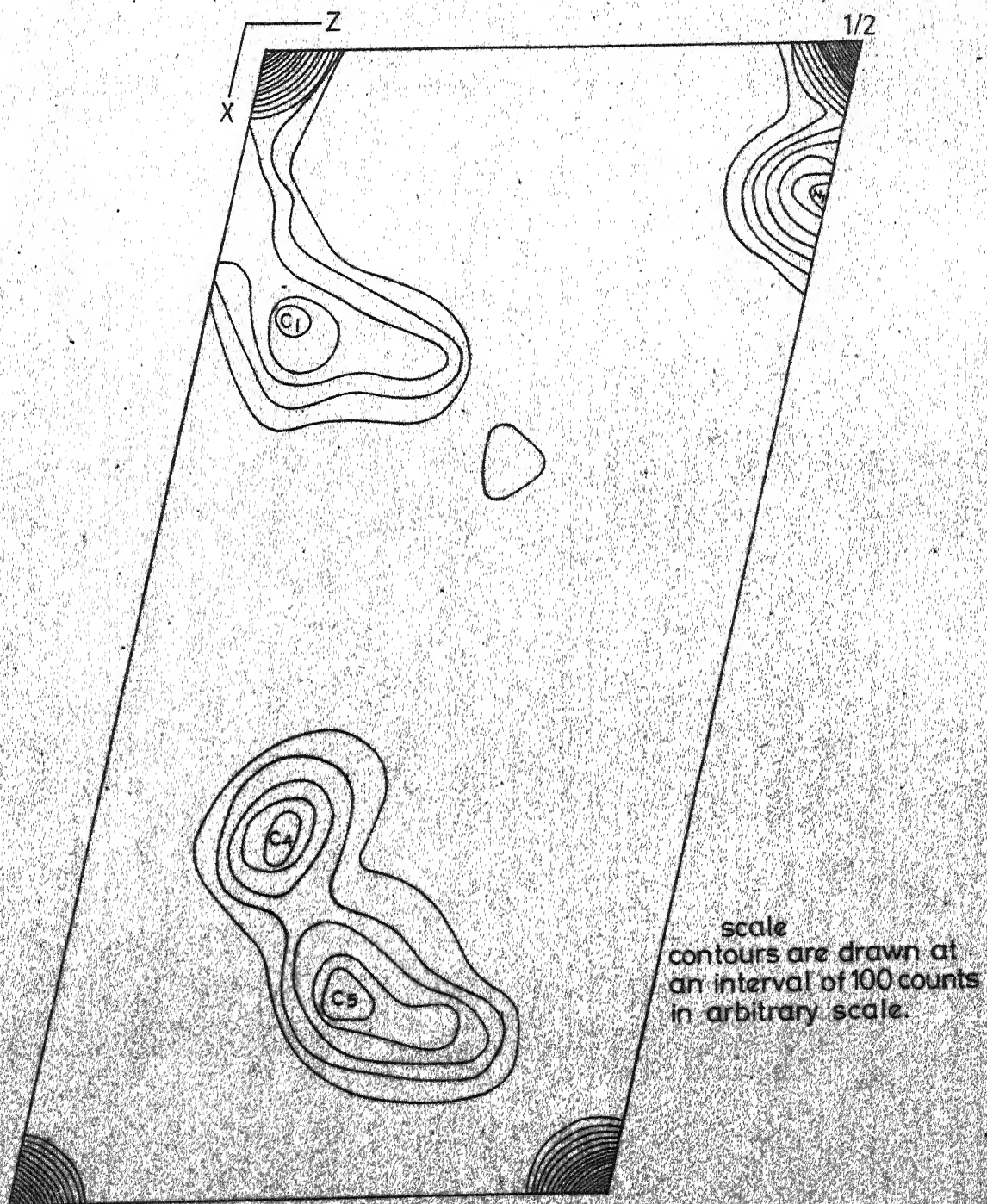


FIG. 3.3b ELECTRON DENSITY CONTOURS AT $Y = 1/4$ IN Bis-(H-PYRROLE
-2 - ALDIMINE) Cu II.

TABLE 3.2a

Atomic Positions and Their Standard Deviations ($\times 10^4$)

Atom	x/a	y/b	z/c
Cu ⁺⁺	0	0	0
N(1)	1287(10)	2648(17)	-160(10)
N(2)	1492(9)	-875(15)	1629(8)
C(1)	2482(14)	2543(23)	813(13)
C(2)	2600(11)	644(17)	1798(11)
C(3)	3687(12)	-78(27)	2931(13)
C(4)	3199(14)	-2213(25)	-3474(14)
C(5)	1829(14)	-2603(23)	2641(13)
H(1)	1290	2890	-260
H(2)	2560	2790	770
H(3)	3800	60	2960
H(4)	3210	-2380	3570
H(5)	1730	-2850	2690

TABLE 3.2b

Anisotropic Temperature Parameters and Their Standard Deviations ($\times 10^4$)

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu ⁺⁺	156 (2)	316 (7)	129 (3)	-32 (5)	37 (2)	-7 (5)
N(1)	161(14)	334(37)	142(13)	-52(19)	33(11)	9(19)
N(2)	120(12)	226(31)	112(11)	-5(15)	28 (9)	-12(15)
C(1)	160(18)	460(55)	168(19)	-47(26)	53(15)	-33(27)
C(2)	123(15)	275(44)	115(14)	3(18)	32(10)	-28(17)
C(3)	174(17)	431(49)	180(18)	53(35)	48(14)	-57(35)
C(4)	183(21)	404(55)	182(20)	28(28)	36(16)	0(28)
C(5)	193(21)	319(52)	148(17)	44(26)	64(15)	14(25)

A calculation for the thermal ellipsoids from the anisotropic temperature parameters was made and the thermal ellipsoids are plotted in Fig. 3.4.

3.3 Discussion

Cu^{++} forms a square planar arrangement with the four nitrogens of the molecule (two from each ligand). Since the molecule has a centre of symmetry at Cu^{++} it lies exactly on the plane formed by $\text{N}(1)$, $\text{N}(2)$, $\text{N}(1)'$ and $\text{N}(2)'$. The bond lengths and the bond angles are shown in Figure 3.5.

The two unique Cu^{++} -N bonds have been found to be 1.97 Å and 1.95 Å in length in this structure. These are in good agreement with Cu-N bonds found in similar structures e.g. 1.97 Å and 1.98 Å in $(\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br})\text{Br}$, 1.98 Å and 1.99 Å in $(\text{Cu}(\text{en})_2(\text{H}_2\text{O}_2)\text{Cl})\text{Cl}$ Mazzi⁽²⁰⁾; 2.01 Å and 2.02 Å in $\text{Cu}(\text{en})_2(\text{NO}_3)_2$ Komiyama and Lingafelter⁽²¹⁾, 1.97 Å and 2.04 Å in $\text{K}_2\text{Cu}(\text{NH}_2\text{CH}_2\text{CONCH}_2\text{COO})_2 \cdot 6\text{H}_2\text{O}$ Sugihara, Ashida, Sasada and Kakudo⁽²²⁾ and 1.99 Å and 2.02 Å in $\text{Cu}(\text{en})_2(\text{SCN})_2$ Brown and Lingafelter⁽²³⁾.

The $\text{N}(1)$ -Cu-N(2) angle of 82.3° in the present structure compares well with 83° in $\text{K}_2\text{Cu}(\text{NH}_2\text{CH}_2\text{CONCH}_2\text{COO})_2 \cdot 6\text{H}_2\text{O}$ Sugihara et.al⁽²²⁾ 85° in $\text{Cu}(\text{en})_2(\text{SCN})_2$ Brown et.al⁽²³⁾ 86° in $\text{Cu}(\text{en})_2(\text{NO}_3)_2$ Komiyama⁽²¹⁾ et.al 86° in $\text{Cu}(\text{en})_2(\text{BF}_4)_2$ Brown, Lee and Melson⁽²⁴⁾, 89° in $(\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl})\text{Cl}$ and 90° in $(\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br})\text{Br}$ by Mazzi et.al⁽²⁰⁾.

In the present structure both the carbons of the ring formed by Cu^{++} , $\text{N}(1)$, $\text{N}(2)$, $\text{C}(1)$ and $\text{C}(2)$ are above the $\text{N}(1)$ - Cu^{++} - $\text{N}(2)$ plane by

TABLE 3.3

Bond Lengths and Bond Angles and Their Standard Deviation

Lengths in Å ($\sigma \times 10^3$)		Angles in degrees	
$\text{Cu}^{++} - \text{N}(1)$	1.972 (9)	$\text{N}(2) - \text{Cu}^{++} - \text{N}(1)$	82.4(0.3)
$\text{Cu}^{++} - \text{N}(2)$	1.950 (8)	$\text{Cu}^{++} - \text{N}(1) - \text{C}(1)$	113.3(0.8)
$\text{N}(1) - \text{C}(1)$	1.328(14)	$\text{N}(1) - \text{C}(1) - \text{C}(2)$	115.6(1.0)
$\text{N}(2) - \text{C}(2)$	1.360(12)	$\text{C}(2) - \text{N}(2) - \text{Cu}^{++}$	112.3(0.6)
$\text{N}(2) - \text{C}(5)$	1.353(15)	$\text{C}(5) - \text{N}(2) - \text{C}(2)$	107.2(0.8)
$\text{C}(1) - \text{C}(2)$	1.406(16)	$\text{N}(2) - \text{C}(2) - \text{C}(3)$	111.4(0.9)
$\text{C}(2) - \text{C}(3)$	1.401(15)	$\text{C}(2) - \text{C}(3) - \text{C}(4)$	105.2(0.9)
$\text{C}(3) - \text{C}(4)$	1.424(19)	$\text{C}(3) - \text{C}(4) - \text{C}(5)$	106.0(1.1)
$\text{C}(4) - \text{C}(5)$	1.421(16)	$\text{C}(4) - \text{C}(5) - \text{N}(2)$	110.1(1.0)
		$\text{C}(1) - \text{C}(2) - \text{N}(2)$	116.4(0.9)

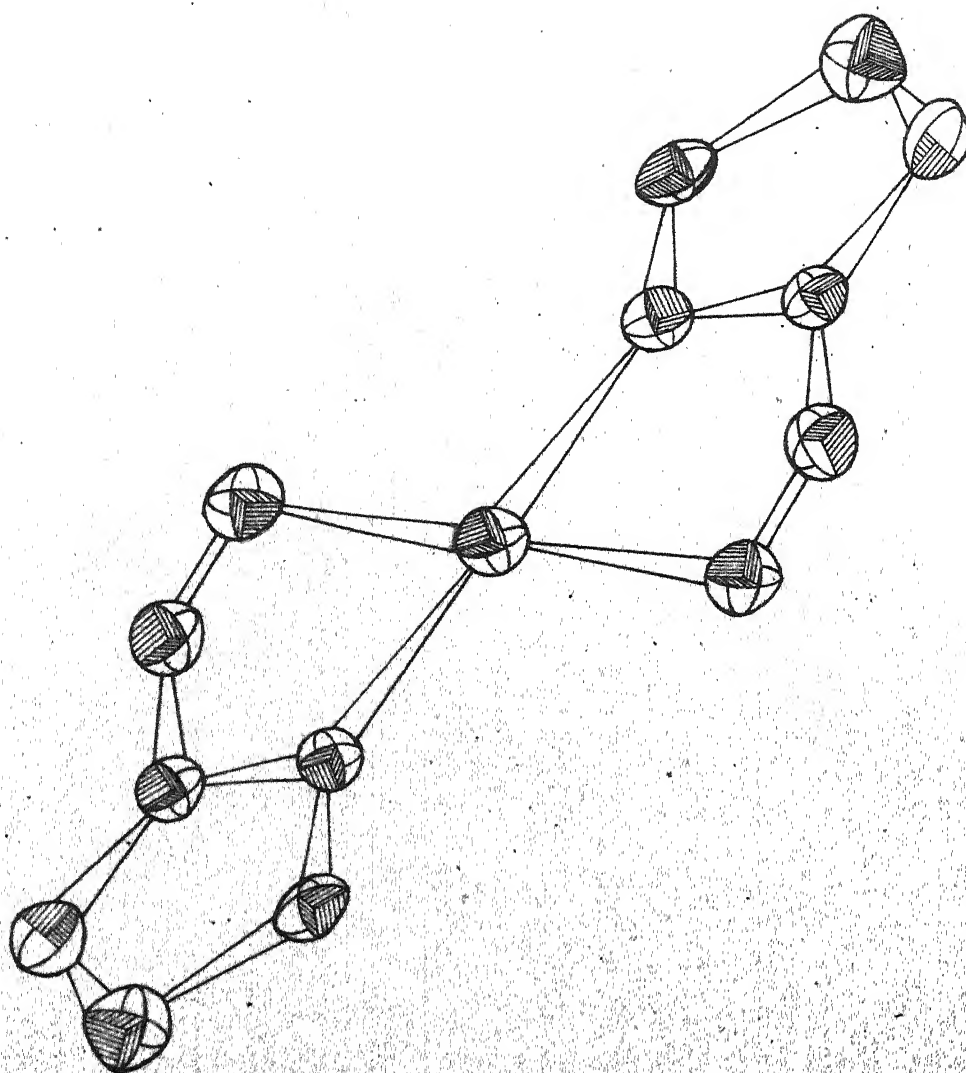


FIG.3.4 X - Z PROJECTION OF THE MOLECULE
SHOWING THERMAL ELLIPSOIDS.

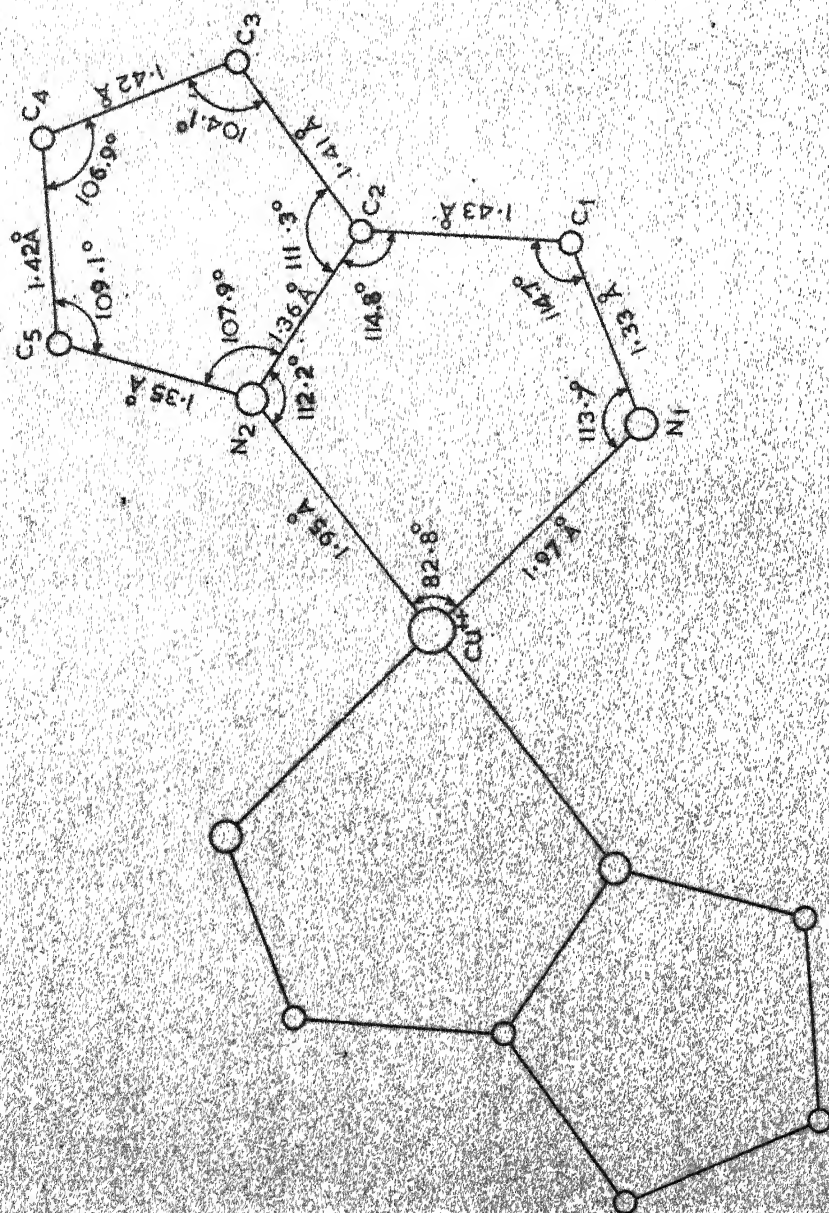


FIG. 3.5 BOND LENGTHS AND ANGLES FOR BIS-(H-PYRROL -
2-ALDIMINE) Cu II.

TABLE 3.4

Deviations of the Atoms From the Best Least Square Plane eqn.(3.1)

Atom	Deviation (\AA)
Cu ⁺⁺	0.0
N(1)	0.018
N(2)	0.063
C(1)	0.010
C(2)	0.020
C(3)	-0.012
C(4)	-0.035
C(5)	0.015

0.098 Å and 0.054 Å. A similar case is that of $K_2Cu(NH_2CH_2CONCH_2COO)_2 \cdot 6H_2O$ Sugihara et.al⁽²²⁾ in which the two carbons of the ethelenediamine ring are above the N-Cu-N plane by 0.406 Å and 0.302 Å. However, in $Cu(en)_2(SCN)_2$ Brown et.al⁽²³⁾ one carbon of the ethelenediamine ring is above the N-Cu-N plane by 0.16 Å and the other is 0.53 Å below the plane. Similarly in $Cu(en)_2(NO_3)_2$ Komiyama et.al⁽²¹⁾ the two carbons are at + 0.39 Å and -0.19 Å from the N-Cu-N plane. In $Cu(en)_2Hg(SCN)_4$ Scouldi⁽²⁵⁾, these distances are + 0.37 Å and -0.68 Å and in $Cu(en)_2(BF_4)_2$ Brown et.al⁽²⁴⁾ these distances are + 0.40 Å and -0.32 Å.

Bis(H-pyrrole-2-alimine)Cu II molecules in the present structure are essentially planar with maximum deviation of 0.06 Å from the least square plane. The equation of the least square plane in the orthogonal angstrom space is:

$$-0.4042 x + 0.5647 y + 0.7195 z = 0 \quad \dots(3.1)$$

The deviation of each atom from this plane is listed in Table 3.4. The equation of the plane containing Cu^{++} , N(1), N(2), N(1)' and N(2)' is

$$-0.4222 x + 0.5647 y + 0.7092 z = 0 \quad \dots(3.2)$$

Pyrrole ring in the present structure is planar with an average bond angle of 108°, average N-C bond-length of 1.355 Å and average C-C bond-length of 1.415 Å. This compares well with the pyrrole rings in tetraphenyl porphyrine (Silvers and Tulinsky⁽²⁶⁾) with an average bond angle of 108°, average N-C bond length of 1.37 Å and average C-C bond length of 1.41 Å. These can also be compared with the pyrrole ring in Ibogaine

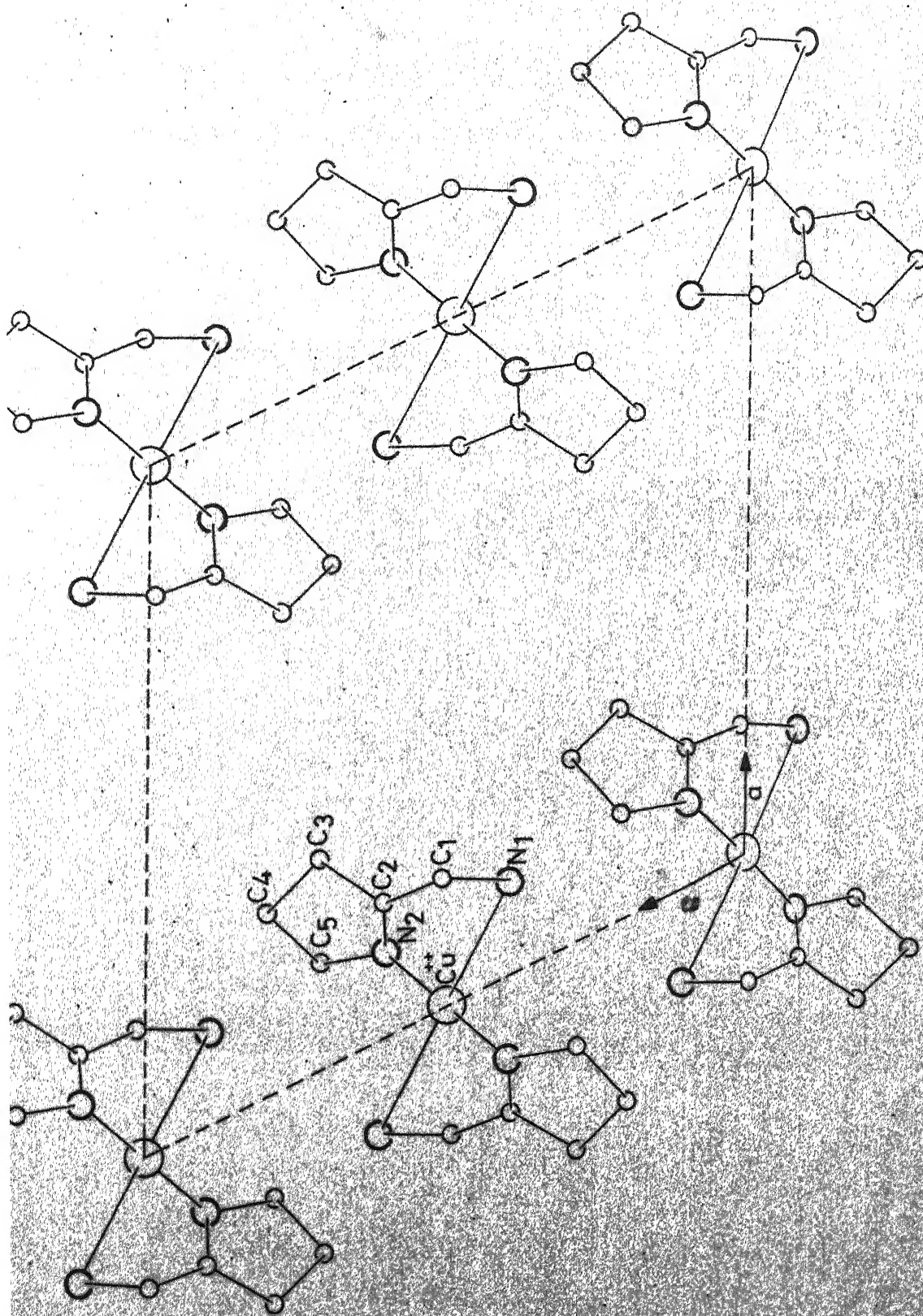


FIG. 3.6 X- \bar{z} PROJECTION OF BIS (H-PYRROLE-2-ALDIMINE) Cu II SHOWING PACKING IN A UNIT CELL.

(Arai, Coppala and Jeffery⁽²⁷⁾) with an average bond-angle of 108° , average N-C bond length of 1.39 \AA and average C-C bond length of 1.43 \AA . The pyrrole ring in Ni II (2,4-diacetyldeutroporphyrin) IX dimethyl ester by Hamor, Caughey and Hoard⁽²⁸⁾ has average bond angle of 107.6° , average N-C bond length of 1.38 \AA and average C-C bond length of 1.41 \AA . The pyrrole ring of Methoxyiron (III)-Mesoporphyrin IX dimethyl ester by Hamor and Hamor⁽²⁹⁾ also has an average bond angle of 108° , average N-C bond length of 1.398 \AA and average C-C bond of 1.420 \AA .

The structure and packing of the molecules in the unit cell has been shown in Fig. 3.6.

TABLE 3.5

Observed and Calculated Structure Factors

* Indicates the Unobserved Reflections

H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC
1	0	0	693	693	9	0	4	56	68
2	0	0	234	286	-9	0	4	67	58
3	0	0	207	222	-10	0	4	87	71
4	0	0	119	142	0	0	6	371	368
5	0	0	206	232	1	0	6	302	297
6	0	0	287	275	-1	0	6	232	231
7	0	0	235	241	2	0	6	200	204
8	0	0	216	210	-2	0	6	188	174
9	0	0	75	62	3	0	6	214	209
10	0	0	26	2*	-3	0	6	119	124
0	0	2	155	159	-4	0	6	166	151
1	0	2	459	478	-5	0	6	180	175
-1	0	2	796	805	6	0	6	113	97
2	0	2	296	300	-6	0	6	173	168
-2	0	2	916	952	7	0	6	88	94
3	0	2	476	446	-7	0	6	166	201
-3	0	2	103	110	-8	0	6	134	127
4	0	2	388	418	-9	0	6	57	53
-4	0	2	215	238	-10	0	6	42	34
5	0	2	46	40	0	0	8	109	108
-5	0	2	294	292	1	0	8	140	124
6	0	2	146	145	-1	0	8	193	194
-6	0	2	89	80	2	0	8	111	114
7	0	2	230	206	-2	0	8	205	205
-7	0	2	125	123	3	0	8	45	54
8	0	2	84	74	-3	0	8	128	113
-8	0	2	220	214	4	0	8	65	70
9	0	2	57	51	-4	0	8	27	23*
-9	0	2	208	201	5	0	8	69	69
10	0	2	60	53	-5	0	8	83	76
-10	0	2	67	64	-6	0	8	177	172
0	0	4	419	421	-7	0	8	95	103
1	0	4	416	397	-8	0	8	50	52
-1	0	4	492	503	-9	0	8	24	61*
2	0	4	578	566	0	0	10	59	58
-2	0	4	152	155	1	0	10	105	116
3	0	4	177	179	-1	0	10	26	14*
-3	0	4	150	137	-2	0	10	46	45
4	0	4	69	77	-3	0	10	43	117
-4	0	4	218	205	-4	0	10	98	102
5	0	4	190	180	-5	0	10	67	68
-5	0	4	326	330	-6	0	10	34	42
6	0	4	78	58	1	1	0	27	24
-6	0	4	340	352	2	1	0	104	112
7	0	4	59	60	3	1	0	46	36
-7	0	4	157	152	4	1	0	18	14*
8	0	4	116	103	5	1	0	152	151
-	-	-	56	58	6	1	0	60	55

table 3.3 contd.

7	1	0	160	164	-2	1	3	692	624
8	1	0	27	19*	3	1	3	428	439
9	1	0	28	42*	-3	1	3	548	529
10	1	0	26	13*	4	1	3	218	219
0	1	1	538	540	-4	1	3	225	243
1	1	1	129	127	5	1	3	208	214
-1	1	1	948	983	-5	1	3	316	312
2	1	1	420	429	6	1	3	194	173
-2	1	1	290	297	-6	1	3	183	182
3	1	1	263	268	7	1	3	29	27
-3	1	1	289	327	-7	1	3	80	95
4	1	1	329	328	-8	1	3	106	94
-4	1	1	340	369	8	1	3	28	40*
5	1	1	312	304	9	1	3	77	70
-5	1	1	190	184	-9	1	3	80	84
6	1	1	198	198	-10	1	3	103	95
-6	1	1	195	208	0	1	4	37	54
7	1	1	206	206	1	1	4	24	49
-7	1	1	173	161	-1	1	4	33	33
8	1	1	95	81	-2	1	4	25	20
-8	1	1	159	154	-2	1	4	20	16*
-9	1	1	94	119	3	1	4	49	54
-10	1	1	26	23*	-3	1	4	177	176
10	1	1	25	37*	4	1	4	73	83
0	1	2	267	264	-4	1	4	39	27
1	1	2	287	291	5	1	4	43	44
-1	1	2	641	617	-5	1	4	158	149
2	1	2	46	49	1	1	4	90	88
-2	1	2	618	596	-6	1	4	77	61
3	1	2	205	184	-7	1	4	26	17*
-3	1	2	187	172	7	1	4	28	12*
4	1	2	45	52	-8	1	4	27	27*
-4	1	2	280	290	8	1	4	26	11*
5	1	2	141	136	-9	1	4	28	19*
-5	1	2	108	117	9	1	4	23	3*
6	1	2	75	90	-10	1	4	44	47
-7	1	2	25	32*	0	1	5	304	291
7	1	2	27	26*	1	1	5	444	412
-8	1	2	27	10*	-1	1	5	232	233
8	1	2	28	0*	2	1	5	221	240
-9	1	2	28	5*	-2	1	5	133	140
9	1	2	27	20*	3	1	5	177	123
-10	1	2	27	12*	-3	1	5	232	228
10	1	2	23	10*	4	1	5	192	189
0	1	3	231	240	-4	1	5	365	352
1	1	3	276	288	5	1	5	83	90
-1	1	3	130	151	-5	1	5	195	198
2	1	3	338	355	6	1	5	58	51

table 3.5 contd.

-6	1	5	194	187	-8	1	8	26	18*
7	1	5	89	89	0	1	9	51	39
-7	1	5	191	178	1	1	9	72	92
8	1	5	66	69	-1	1	9	74	69
-8	1	5	79	67	2	1	9	65	77
-9	1	5	47	39	-2	1	9	146	146
-10	1	5	41	37	3	1	9	59	61
0	1	6	24	17*	-3	1	9	130	124
1	1	6	22	19	-4	1	9	114	102
2	1	6	48	47	-5	1	9	80	77
-2	1	6	109	108	-6	1	9	57	62
-3	1	6	75	68	-7	1	9	25	53*
-4	1	6	113	97	0	1	10	25	13*
-5	1	6	85	85	1	1	10	29	30*
-6	1	6	27	4	-1	1	10	30	33
6	1	6	27	7*	-2	1	10	26	7*
-7	1	6	28	19*	-3	1	10	26	11*
7	1	6	25	16*	-4	1	10	25	6*
-8	1	6	28	11*	-5	1	10	39	38
-9	1	6	27	6*	-6	1	10	38	44
-10	1	6	24	7	0	2	0	162	113
0	1	7	222	222	1	2	0	229	220
1	1	7	73	71	2	2	0	532	542
-1	1	7	276	261	3	2	0	452	469
2	1	7	101	109	4	2	0	246	265
-2	1	7	202	193	5	2	0	252	282
3	1	7	119	123	6	2	0	159	144
-3	1	7	155	149	7	2	0	114	101
4	1	7	68	68	8	2	0	138	118
-4	1	7	109	104	9	2	0	35	36
5	1	7	77	83	10	2	0	24	29*
-5	1	7	158	150	0	2	1	53	68
6	1	7	56	75	1	2	1	117	82
-6	1	7	126	116	-1	2	1	78	9
-7	1	7	54	53	2	2	1	148	152
-8	1	7	116	116	-2	2	1	138	124
-9	1	7	25	70*	3	2	1	59	32
0	1	8	28	52*	-3	2	1	137	131
1	1	8	62	72	4	2	1	133	130
-2	1	8	27	8*	-4	2	1	88	78
2	1	8	28	19*	5	2	1	30	42
3	1	8	78	86	-5	2	1	49	23
-4	1	8	28	13*	6	2	1	72	62
4	1	8	26	21*	-6	2	1	93	82
-5	1	8	28	19*	-7	2	1	26	7*
5	1	8	24	25*	7	2	1	27	27*
-6	1	8	28	20*	-8	2	1	28	25*
7	1	8	27	10*	8	2	1	28	13*

table 3.5 contd.

-9	2	1	27	13*	3	2	4	221	235
9	2	1	27	18*	-3	2	4	657	654
-10	2	1	25	25*	4	2	4	211	223
10	2	1	23	1	-4	2	4	322	323
0	2	2	116	137	5	2	4	181	178
1	2	2	246	235	-5	2	4	95	101
-1	2	2	280	466	6	2	4	57	60
2	2	2	295	290	-6	2	4	159	154
-2	2	2	450	461	7	2	4	46	41
3	2	2	272	270	-7	2	4	93	82
-3	2	2	307	314	8	2	4	69	53
4	2	2	278	277	-8	2	4	86	72
-4	2	2	397	396	-9	2	4	84	65
5	2	2	283	282	-10	2	4	42	47
-5	2	2	213	214	0	2	5	69	66
6	2	2	257	248	1	2	5	52	34
-6	2	2	134	168	-1	2	5	27	31
7	2	2	64	52	2	2	5	49	52
-7	2	2	164	158	-2	2	5	64	60
-8	2	2	28	21*	3	2	5	76	90
8	2	2	28	18*	-4	2	5	112	108
9	2	2	68	46	-5	2	5	40	40
-9	2	2	60	53	6	2	5	36	40
-10	2	2	98	88	-6	2	5	52	55
0	2	3	56	52	-7	2	5	28	45*
1	2	3	50	41	7	2	5	26	4*
-1	2	3	24	32	-8	2	5	28	16*
2	2	3	140	119	-9	2	5	27	1*
-2	2	3	75	79	-10	2	5	24	1*
3	2	3	61	62	0	2	6	248	249
-3	2	3	63	52	1	2	6	170	177
4	2	3	101	86	-1	2	6	222	219
-4	2	3	96	95	-2	2	6	208	213
5	2	3	68	85	3	2	6	106	104
-5	2	3	101	85	-3	2	6	112	112
-6	2	3	25	23	4	2	6	172	173
6	2	3	27	19*	-4	2	6	213	209
-7	2	3	27	22*	5	2	6	84	104
7	2	3	28	9*	-5	2	6	231	222
-8	2	3	28	23*	-6	2	6	68	58
8	2	3	27	14*	-7	2	6	85	91
-9	2	3	27	5*	-8	2	6	112	116
9	2	3	24	4*	-9	2	6	25	28*
-10	2	3	25	7*	0	2	7	27	18*
0	2	4	198	205	-1	2	7	27	5*
1	2	4	270	249	1	2	7	27	27*
2	2	4	278	269	-2	2	7	27	25*
-2	2	4	239	241	2	2	7	28	41*

table 3.5 contd.

-3	2	7	60	54	3	3	1	215	216
-4	2	7	44	47	-3	3	1	254	254
-5	2	7	28	27*	4	3	1	213	219
5	2	7	25	4*	-4	3	1	202	198
-6	2	7	54	58*	5	3	1	143	138
-7	2	7	27	3*	-5	3	1	138	141
-8	2	7	27	22*	6	3	1	99	83
-9	2	7	24	20*	-6	3	1	171	166
0	2	8	46	44	7	3	1	133	120
1	2	8	36	29	-7	3	1	87	87
-1	2	8	168	168	8	3	1	73	73
2	2	8	109	112	-8	3	1	84	83
-2	2	8	140	135	-9	3	1	59	87
3	2	8	80	80	0	3	2	148	134
-3	2	8	150	142	1	3	2	223	229
4	2	8	48	58	-1	3	2	153	166
-4	2	8	168	163	-2	3	2	154	164
-5	2	8	85	78	3	3	2	100	94
-6	2	8	39	40	-4	3	2	24	26*
-7	2	8	26	24*	4	3	2	25	35*
-8	2	8	24	46*	-5	3	2	42	31
0	2	9	26	8*	-6	3	2	27	46*
-1	2	9	27	3*	6	3	2	28	37*
1	2	9	26	4*	-7	3	2	28	34*
2	2	9	22	23*	7	3	2	28	11*
-3	2	9	27	18*	-8	3	2	28	24*
-4	2	9	27	9*	8	3	2	26	6*
-5	2	9	37	36	-9	3	2	26	21*
-6	2	9	25	14*	0	3	3	273	280
-7	2	9	23	16*	1	3	3	301	301
-1	2	10	55	55	-1	3	3	224	210
-2	2	10	74	76	2	3	3	228	219
-3	2	10	78	83	-2	3	3	306	307
-4	2	10	47	45	3	3	3	186	183
1	3	0	42	34	-3	3	3	178	179
2	3	0	207	198	4	3	3	122	118
3	3	0	139	131	-4	3	3	122	125
4	3	0	24	26*	5	3	3	120	115
5	3	0	53	55	-5	3	3	214	217
6	3	0	27	37*	6	3	3	97	106
7	3	0	28	23*	-6	3	3	134	130
8	3	0	27	24*	7	3	3	67	63
9	3	0	62	62	-7	3	3	105	101
0	3	1	368	363	-8	3	3	84	95
1	3	1	275	263	-9	3	3	46	48
-1	3	1	403	384	0	3	4	24	25*
2	3	1	296	275	1	3	4	51	51
-2	3	1	214	216	-1	3	4	39	47

table 3.5 contd.

2	3	4	63	60	-5	3	7	103	112
3	3	4	91	91	-6	3	7	91	102
4	3	4	146	172	-7	3	7	49	45
-5	3	4	27	5*	-8	3	7	60	58
5	3	4	28	20*	0	3	8	27	11*
6	3	4	83	76	-1	3	8	27	1*
-6	3	4	67	63	1	3	8	26	3*
-7	3	4	28	30*	-2	3	8	27	19*
7	3	4	25	26*	2	3	8	25	15*
-8	3	4	27	29*	-3	3	8	27	11*
-9	3	4	25	7*	3	3	8	24	8*
0	3	5	160	170	-4	3	8	50	51
1	3	5	160	165	-5	3	8	33	38
-1	3	5	259	250	-6	3	8	44	48
2	3	5	161	154	-5	3	8	23	23*
-2	3	5	166	161	0	3	9	43	52
3	3	5	112	114	-1	3	9	62	63
-3	3	5	156	149	-2	3	9	92	92
4	3	5	117	127	-3	3	9	54	56
-4	3	5	191	191	-4	3	9	57	52
5	3	5	79	78	-5	3	9	57	50
-5	3	5	72	77	0	4	0	407	393
6	3	5	44	46	1	4	0	225	196
-7	3	5	132	128	2	4	0	100	109
-8	3	5	62	68	3	4	0	172	182
-9	3	5	57	58	4	4	0	140	122
0	3	6	27	33*	5	4	0	138	122
1	3	6	27	12*	6	4	0	94	97
-1	3	6	27	9*	7	4	0	62	60
2	3	6	109	112	8	4	0	71	71
-2	3	6	110	100	0	4	1	25	7*
3	3	6	70	73	1	4	1	37	40
-3	3	6	112	117	-1	4	1	47	54
-4	3	6	75	82	2	4	1	38	39
5	3	6	32	37	-2	4	1	33	38
-5	3	6	136	145	-3	4	1	79	91
-6	3	6	28	3*	4	4	1	48	52
-7	3	6	53	63	-4	4	1	78	81
-8	3	6	42	50	-5	4	1	28	23*
0	3	7	142	146	5	4	1	28	2*
1	3	7	89	95	6	4	1	43	57
-1	3	7	108	108	7	4	1	37	49
2	3	7	98	106	-7	4	1	41	30
-2	3	7	111	101	-8	4	1	25	27*
3	3	7	97	99	8	4	1	23	17*
-3	3	7	136	122	0	4	2	197	195
4	3	7	36	37	1	4	2	372	395
-4	3	7	80	75	-1	4	2	198	191

table 3.5 contd.

2	4	2	181	181	-5	4	5	27	11*
-2	4	2	198	188	5	4	5	24	10*
3	4	2	142	139	-6	4	5	36	34
-3	4	2	85	77	7	4	5	37	14
4	4	2	128	120	0	4	6	74	78
-4	4	2	137	133	1	4	6	108	105
-5	4	2	141	146	-1	4	6	73	73
6	4	2	30	50	2	4	6	115	119
-6	4	2	85	98	-2	4	6	135	125
7	4	2	92	109	3	4	6	106	116
-7	4	2	83	94	-3	4	6	118	107
-8	4	2	70	73	-4	4	6	72	90
0	4	3	26	3*	-5	4	6	72	84
-1	4	3	26	16*	-6	4	6	62	60
1	4	3	27	10*	-7	4	6	59	62
-2	4	3	48	52	0	4	7	26	8*
-3	4	3	45	53	1	4	7	23	33
-4	4	3	27	18*	-2	4	7	27	24*
4	4	3	28	22*	2	4	7	24	29*
5	4	3	57	63	-3	4	7	26	9*
-5	4	3	96	89	-4	4	7	34	46
-6	4	3	53	61	-5	4	7	25	9*
-7	4	3	27	11*	-6	4	7	23	14*
7	4	3	23	2*	0	4	8	68	78
-8	4	3	25	4*	-1	4	8	63	61
0	4	4	224	221	-2	4	8	46	45
1	4	4	105	115	-3	4	8	49	46
-1	4	4	281	276	-4	4	8	41	34
2	4	4	127	138	1	5	0	28	15*
-2	4	4	129	122	2	5	0	28	6*
3	4	4	77	67	3	5	0	37	31
-3	4	4	40	50	4	5	0	27	10*
4	4	4	59	51	5	5	0	26	25*
-4	4	4	54	58	6	5	0	24	29*
5	4	4	89	96	0	5	1	68	61
-5	4	4	121	112	1	5	1	127	126
6	4	4	68	65	-1	5	1	90	107
-6	4	4	144	132	2	5	1	205	207
-7	4	4	75	86	-2	5	1	81	72
-8	4	4	54	75	3	5	1	96	104
0	4	5	28	19*	-3	5	1	134	123
1	4	5	33	35	4	5	1	77	79
-2	4	5	28	28*	-4	5	1	150	157
2	4	5	28	9*	5	5	1	72	76
3	4	5	47	50	-5	5	1	82	98
-4	4	5	28	35*	6	5	1	41	35
4	4	5	26	21*	-6	5	1	70	81

table 3.5 contd.

0	5	2	28	42*	-6	5	4	25	23
-1	5	2	67	64	0	5	5	40	44
2	5	2	27	13*	1	5	5	63	64
-2	5	2	85	91	-1	5	5	90	94
3	5	2	31	31	2	5	5	46	54
-4	5	2	75	72	-2	5	5	106	114
5	5	2	34	53	-3	5	5	90	90
-5	5	2	44	48	-4	5	5	88	89
-6	5	2	25	6*	-5	5	5	61	62
0	5	3	161	171	0	5	6	24	5*
1	5	3	95	95	-1	5	6	24	13*
-1	5	3	92	101	1	5	6	23	3*
2	5	3	57	50	-2	5	6	24	34*
-2	5	3	83	94	-3	5	6	24	7*
3	5	3	90	94	0	6	0	25	4*
-3	5	3	104	107	1	6	0	37	40
4	5	3	57	60	2	6	0	118	121
-4	5	3	71	74	3	6	0	108	109
5	5	3	53	61	0	6	1	25	9*
-5	5	3	78	77	-1	6	1	25	8*
-6	5	3	67	72	1	6	1	24	14*
0	5	4	27	37*	2	6	1	30	34
-1	5	4	27	3*	-3	6	1	23	1*
1	5	4	27	20*	0	6	2	69	76
-2	5	4	27	20*	1	6	2	134	103
2	5	4	26	17*	-1	6	2	40	49
-3	5	4	38	31	-2	6	2	45	44
-4	5	4	26	6*	-1	6	3	26	40
4	5	4	26	6*					
-5	5	4	39	46					

CHAPTER IV

CRYSTAL STRUCTURE OF $\text{Cu}(\text{Sal})(\text{SalNMe}_2)$ 4.1 Experimental

Crystals of $\text{Cu}(\text{Sal})(\text{SalNMe}_2)$ are obtained by reacting bis(salicylaldehyde)Cu II, $\text{Cu}(\text{Sal})_2$ with N,N-dialkylethylenediamine in the stoichiometric ratio in boiling toluene⁽³⁰⁾. The crystals are green in colour. A crystal of suitable size was chosen for X-Ray studies.

Preliminary studies were done photographically with the help of rotation and Weissenberg photographs. The crystals were found to belong to the monoclinic ^{system} ~~class~~. Rotation and Weissenberg photographs of o-layer, I layer and II layer were taken from a crystal mounted along b unique axis. $\text{CuK}\alpha$ radiation with Ni filter was used. The following systematic absences were observed:

1. hkl reflections present only when $h+k=2n$
2. hol reflections present only when $h=2n$ and $l=2n$
3. oko reflections present only when $k=2n$.

These systematic absences point to the space group being either C_{2h} C_c or C_2/c or C_c . These two space groups are different only in the sense that C_2/c has a centre of symmetry while C_c does not.

The crystal was then transferred to a General Electric XRD-6 Diffractometer equipped with eulerian cradle. The lattice constants a , b , c , and β were accurately determined by the method discussed in Chapter 3. The lattice parameters are listed in table 4.1.

TABLE 4.1

Crystal Data Cu(Sal)(SalNMe₂)

Chemical Formula	C ₁₈ H ₂₀ N ₂ O ₃ Cu melting pt. 208° ± 9°C
Molecular weight	375.90
Calculated Density	1.49 gm/cm ³
Measured Density	1.45 ± .04 gm/cm ³

Monoclinic Unit Cell Dimensions

$$a = 18.11 \pm .02 \text{ \AA}$$

$$b = 11.24 \pm .03 \text{ \AA}$$

$$c = 16.77 \pm .02 \text{ \AA}$$

$$\beta = 94^\circ \pm .02^\circ$$

$$\text{volume of the unit cell} = 3350.4 \text{ \AA}^3$$

Systematic Absences

hkl present when $h+k=2n$

hol present when $h=2n$ and $l=2n$

oko present when $k=2n$

Space group ~~C_{2h}~~ or ~~C_2~~ C_{2h} or C_c

No. of molecules in unit cell = 8

The angular settings ϕ , χ and 2θ of the goniostat for all the hkl and $\bar{h}kl$ reflections in the $\text{CuK}\alpha$ sphere of reflection were calculated by a computer program described in appendix 1.

Three dimensional intensity data was collected using stationary crystal stationary counter technique, as described in Chapter 3. A total of 1703 reflections were observed and their intensities were recorded. There were 359 reflections whose peak counts were within one standard deviation of the background. These reflections have been classified as unobserved.

The intensities of ten reflections viz., 400, 408, 808, 111, 624, 424, 4210, 1224, 226, 643 and 150 were monitored every 24 hours as a check against possible mis-alignment of the crystal, instrumental fault or radiation damage to the crystal. The reflections with very high intensity (those which count more than 2000 counts per second) were recorded with additional Ni absorbers. The filter factor for these were determined experimentally. The intensity data beyond the 2θ angle of 90° was not collected because more than two thirds of the reflections in this region had intensity almost equal to the background.

Lorentz, Polarization and the background corrections to the intensity data were applied through the computer program described in appendix 2. The correction due to absorption was checked for 020, 040, 060, 080. and 0100 reflections at $\chi = 90^\circ$ in the manner described in Chapter 3 and the correction due to absorption for the crystal used was found to be small. The absorption correction was therefore neglected.

4.2 Crystal Structure Determination

The systematic absences indicate that the crystals of $\text{Cu}(\text{Sal})(\text{SalNMe}_2)$ belong to the space group $C_{2/c}$ or C_c . To resolve this ambiguity a $Z - N(z)^{(31)}$ plot to test for the centre of symmetry was done. However, the $z - N(z)$ plot showed too much of scatter and there was no clear indication for the presence or absence of the centre of symmetry. The space group was therefore assumed as $C_{2/c}$ and the structure could be solved and refined in this space group. The choice of the space group was thus confirmed. The space group $C_{2/c}$ has eight equivalent positions and since the crystal has eight molecules per unit cell, there is only one molecule in the asymmetric unit.

Heavy atom method with Patterson synthesis has successfully been applied for solving this structure. A three dimensional Patterson's synthesis was done for locating the heavy atom and Harker line and sections were scanned for strong peaks due to Cu - Cu vectors. The Harker line $(0, 2y, \frac{1}{2})$ showed a very strong peak at $(0, \frac{36}{60}, \frac{1}{2})$. The y co-ordinate of the heavy atom (Cu in this case) was thus calculated as $\frac{18}{60}$. For x and z co-ordinates of Cu, the Harker sections of the type $(2x, 0, 2z - \frac{1}{2})$ were scanned for strong peaks. The x and z co-ordinates of Cu were calculated from a strong peak located at $(\frac{54}{60}, 0, \frac{3}{4})$, as $\frac{27}{60}$ and $\frac{7.5}{60}$.

The position of the Cu atom thus being fixed, a structure factor calculation was done using an overall temperature factor of 4.0. The value of the reliability index R obtained was 51.0%. A three dimensional fourier synthesis was done with the phases calculated on the basis of Cu atom. This synthesis showed several peaks. Three good peaks were chosen and were assigned to atoms O(2), O(3) and N(1) on the basis of Cu-O and Cu-N

bond lengths and angles. A structure factor calculation with four atoms viz., Cu, O(2), O(3) and N(1), using an overall temperature factor of 4.0 was done and a R value of 46.7% was obtained.

A three dimensional fourier synthesis with the phases due to above mentioned atoms revealed seven more atoms, viz., C(1), C(2), C(3), C(6), C(7), C(8) and C(9). Structure factor calculation with these eleven atoms with an overall temperature factor 4.0 gave a R value of 39.0%.

At this stage the individual isotropic temperature factor were introduced. These temperature factors were obtained from two successive Fo and difference syntheses. A structure factor calculation with the eleven atoms and these isotropic temperature factors yielded a R value of 36%.

The above Fo synthesis gave the positions of nine more atoms making the total numbers of atoms assigned so far as twenty. These newly found atoms were assigned isotropic temperature factor of 4.0 equal to the overall temperature factor and a structure factor calculation was done. The value of R obtained was 32%.

The position as well as the isotropic temperature parameters of these twenty atoms were then refined by two successive Fo and difference fourier syntheses and structure factor calculation with refined parameters gave the value of R as 28%. The only atoms not located so far were C(15), C(16), C(17) and C(18). These were finally picked up from the three dimensional Fo synthesis calculated with the phases due to 20 atoms. The molecule thus formed looked chemically reasonable. A structure factor calculation with all the 24 atoms of the molecule included gave R = 23%.

4.3 Refinement

The position parameters of all the atoms in the asymmetric unit and the scale constant were refined by full matrix least square calculation using the adapted version of the computer program ORFLS⁽³²⁾. Five cycles of refinement brought the R to 19.8% and the shifts in position parameters were very small indicating saturation in refinement. The isotropic temperature factor parameters of all the atoms were now varied along with the position parameters through four cycles and at the end of fourth cycle the value of R was 14.1%.

The individual isotropic temperature factor parameters were now converted to anisotropic temperature factors of the form:

$$\exp \left[-\frac{1}{2} \left(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2kl \beta_{23} + 2hl \beta_{13} \right) \right]$$

The full matrix least square refinement program (ORFLS)⁽³²⁾ can vary only 100 parameters at a time and this structure has a total of 218 parameters to be varied. Hence to start with the anisotropic temperature parameters of half the molecule were refined while holding the others constant. Two cycles of least square refinement yielded a R value of 12.5%. Now these refined parameters were held constant and the anisotropic temperature parameters of the rest of the molecule were refined through two cycles of least square refinement which gave a R value of 11.7% on all the observed reflections.

Finally in order to saturate the parameters several cycles of least square refinement were run varying 100 parameters at a time. First 100

parameters including the scale constant, position and anisotropic temperature parameters were refined holding the rest of them constant and later, those varied were held constant and the rest of them were refined till the final shifts for all the parameter became less than $\frac{1}{4}\sigma$ (i.e. one fourth of standard deviation) for that parameter. The final value of R for all the observed reflections was 11.0%. The value of R with the unobserved reflections included is 14.4%.

The final position parameters with their standard deviations are listed in Table 4.2a and the thermal parameters are listed in Table 4.2b. The bond lengths, and bond angles with their standard deviations are listed in Tables 4.3a and 4.3b respectively. Fig. 4.1 shows the X-Y projection of the molecule showing the thermal ellipsoids. Fig. 4.2a is a X-Y projection showing bond lengths and Fig. 4.2b shows the bond angles.

4.4 Discussion

Cu atom is coordinated to five atoms N(1), N(2), O(1), O(2) and O(3). This penta coordination is a distorted square pyramid with N(1), N(2), O(2) and O(3) forming the base and O(1) at the apex. The X-Y projection of the coordination polyhedra of two complex molecules as they exist in a unit cell are shown in Fig. 4.3. They can be distinguished by the dotted and full lines. The atom N(1) of one molecule and the corresponding N(1)' of the other molecule have the same X-Y coordinate and differ in Z coordinate only. The basal plane of the square pyramids are facing each other while the apex are in opposite directions.

TABLE 4.2a

Position Parameter Table

Atom	$\frac{X}{a} \times 10^4$	$\frac{Y}{b} \times 10^4$	$\frac{Z}{c} \times 10^4$
C(7)	3544(8)	0996(14)	0843(10)
C(2)	3275(8)	1339(14)	0088(8)
C(17)	5800(15)	1554(27)	1661(13)
C(18)	5394(12)	1447(21)	282(13)
C(2)	3977(6)	1527(9)	1355(6)
H(2)	5474(6)	2156(11)	997(7)
C(1)	3521(8)	2459(17)	-286(10)
Su	4495(1)	2996(2)	1254(1)
O(1)	4012(6)	3135(8)	-6(6)
C(16)	6022(14)	2974(24)	1011(27)
H(1)	5096(6)	4426(10)	1220(7)
C(5)	2805(8)	-777(16)	605(10)
C(15)	5821(8)	4196(15)	891(10)
C(3)	2767(8)	727(14)	-419(10)
O(3)	3718(7)	3747(13)	1795(7)
C(8)	3662(9)	4901(19)	1957(10)
C(9)	3013(9)	5252(17)	2341(9)
C(14)	4912(9)	5459(15)	1443(9)
C(13)	4208(18)	5732(16)	1787(9)
C(10)	2913(11)	6406(18)	2537(10)
C(11)	3462(10)	7233(17)	2348(11)
C(12)	4078(11)	6890(15)	1973(10)
C(4)	2538(9)	-340(16)	-131(11)
C(6)	2581(8)	-114(14)	1110(9)

TABLE 4.2b

Thermal Parameters $\times 10^5$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(7)	157(54)	774(173)	418(82)	-1(81)	64(54)	-175(103)
C(2)	238(59)	1025(195)	244(71)	108(84)	-12(51)	0(93)
C(17)	965(137)	3309(54)	701(142)	970(193)	-118(113)	552(227)
C(18)	625(111)	2386(385)	642(118)	245(164)	27(88)	-602(179)
O(2)	355(45)	480(106)	484(55)	-251(55)	6(41)	118(60)
N(2)	287(52)	390(123)	552(69)	-57(66)	39(47)	-216(79)
C(1)	331(71)	898(200)	431(85)	-64(100)	61(62)	-127(105)
Cu	389(10)	627(24)	464(12)	-86(11)	20(7)	-54(12)
O(1)	364(46)	511(103)	562(59)	-58(60)	40(42)	30(63)
C(16)	653(138)	1394(355)	3564(477)	147(196)	859(208)	-303(358)
N(1)	304(50)	459(127)	499(64)	-324(56)	22(44)	34(71)
C(5)	282(64)	1229(213)	541(87)	-131(98)	-27(59)	-48(112)
C(15)	312(63)	848(190)	717(101)	-35(89)	159(63)	-30(110)
C(3)	288(63)	874(180)	618(91)	127(87)	8(59)	151(103)
O(3)	359(43)	817(112)	523(54)	-88(55)	135(38)	-47(64)
C(8)	376(74)	1029(177)	391(79)	-49(114)	-45(60)	131(111)
C(9)	354(76)	1484(259)	392(79)	162(107)	12(61)	-147(112)
C(14)	522(82)	629(181)	489(83)	-280(98)	-92(67)	-81(97)
C(13)	461(79)	709(196)	297(69)	109(102)	86(58)	33(90)
C(10)	633(98)	889(217)	450(87)	190(121)	15(72)	118(114)
C(11)	584(90)	965(218)	513(92)	84(120)	154(75)	145(115)
C(12)	642(97)	860(224)	419(80)	-76(121)	-40(67)	106(99)
O(4)	282(61)	1340(222)	635(95)	-207(96)	33(60)	-136(120)
C(6)	354(63)	656(161)	515(79)	3(81)	99(56)	-108(91)

TABLE 4.3a

Table Showing the Bond Lengths in Å ($\sigma \times 10^2$)

Bond	Bond-length	Bond	Bond-length
Cu -N(1)	1.94(1)	O(3) -C(8)	1.33(3)
Cu -N(2)	2.08(1)	C(8) -C(9)	1.43(2)
Cu -O(2)	1.91(1)	C(8) -C(13)	1.40(2)
Cu -O(3)	1.92(1)	C(9) -C(10)	1.35(3)
Cu -O(1)	2.23(1)	C(10)-C(11)	1.41(3)
C(1)-C(1)	1.24(2)	C(11)-C(12)	1.37(3)
C(1)-C(2)	1.49(2)	C(12)-C(13)	1.36(2)
C(2)-C(3)	1.39(2)	C(13)-C(14)	1.47(2)
C(2)-C(7)	1.38(2)	C(14)-N(1)	1.27(2)
C(3)-C(4)	1.37(2)	N(1) -C(15)	1.48(2)
C(4)-C(5)	1.44(2)	C(15)-C(16)	1.43(3)
C(5)-C(6)	1.30(2)	C(16)-N(2)	1.35(3)
C(6)-C(7)	1.41(2)	N(2) -C(17)	1.40(3)
C(7)-O(2)	1.27(2)	N(2) -C(18)	1.44(2)

TABLE 4.3b

Table of Bond Angles in Degrees ($\sigma \times 10$)

Bond	Bond-angle	Bond	Bond-angle
O(1)-Cu -O(3)	99.5(5)	Cu -O(3) -C(8)	126.4(11)
O(1)-Cu -N(2)	96.8(4)	O(3) -C(8) -C(13)	122.8(15)
O(1)-Cu -O(2)	89.0(4)	C(8) -C(13)-C(14)	125.7(16)
O(1)-Cu -N(1)	95.6(4)	C(13)-C(14)-N(1)	124.0(15)
N(1)-Cu -N(2)	83.2(4)	C(14)-N(1) -Cu	126.0(10)
O(3)-Cu -N(1)	90.6(5)	C(13)-C(8) -C(9)	121.2(18)
O(2)-Cu -N(2)	93.2(4)	C(8) -C(9) -C(10)	120.0(17)
O(3)-Cu -O(2)	87.6(5)	C(9) -C(10)-C(11)	117.9(17)
Cu -O(1)-C(1)	122.7(10)	C(10)-C(11)-C(12)	121.6(17)
O(1)-C(1)-C(2)	126.0(14)	C(11)-C(12)-C(13)	122.1(17)
C(1)-C(2)-C(7)	121.7(13)	C(12)-C(13)-C(8)	117.0(16)
C(2)-C(7)-O(2)	130.7(15)	Cu -N(1) -C(15)	112.3(9)
C(7)-O(2)-Cu	129.0(10)	N(1) -C(15)-C(16)	109.7(16)
C(7)-C(2)-C(3)	126.8(14)	C(15)-C(16)-N(2)	118.1(19)
C(2)-C(3)-C(4)	114.9(15)	C(16)-N(2) -Cu	108.8(13)
C(3)-C(4)-C(5)	117.8(15)	C(16)-N(2)--C(17)	92.7(21)
C(4)-C(5)-C(6)	123.9(17)	C(17)-N(2) -C(18)	114.0(17)
C(5)-C(6)-C(7)	118.1(15)	C(18)-N(2) -Cu	112.7(10)
C(6)-C(7)-C(2)	115.9(14)		

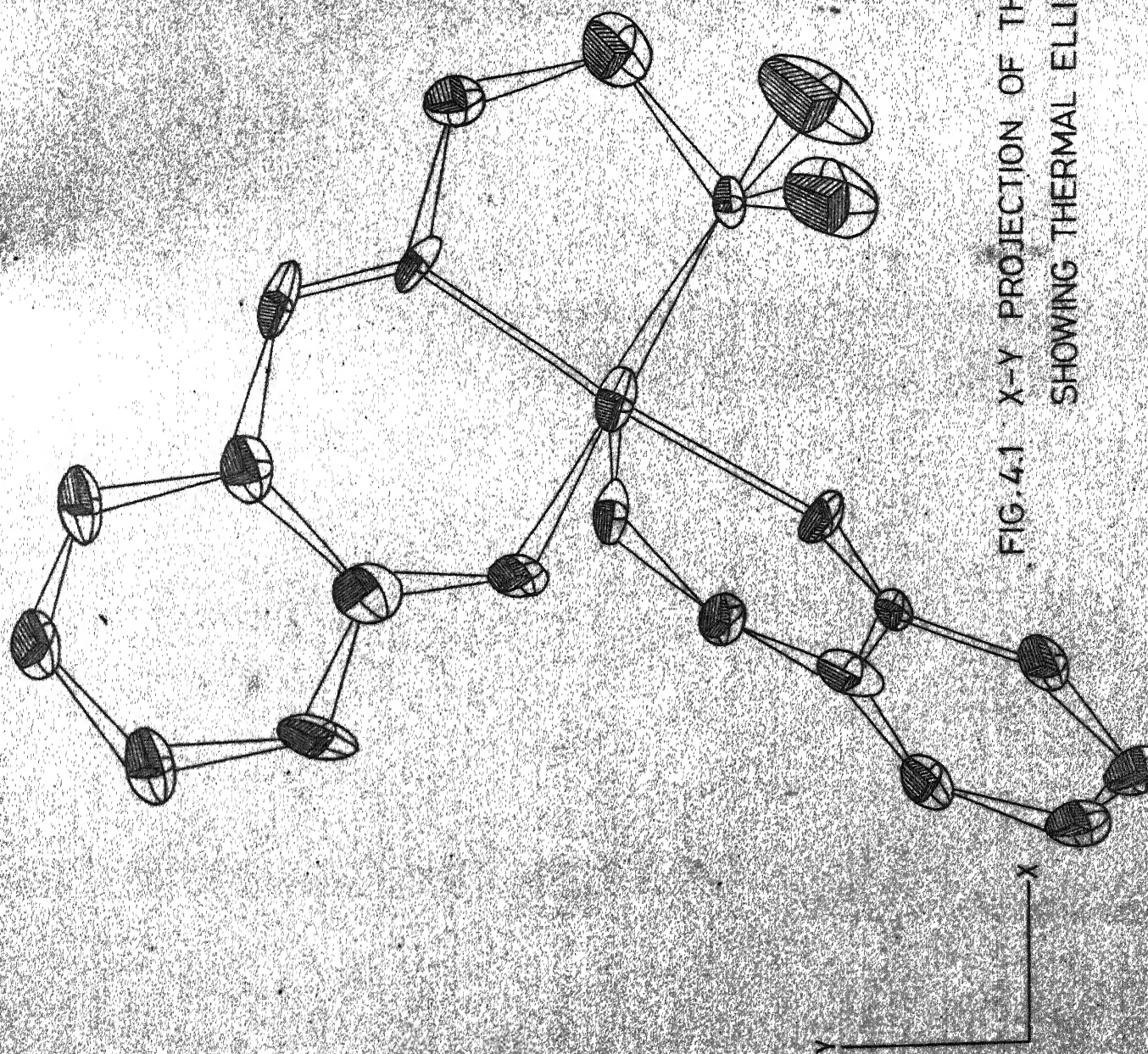


FIG. 4.1 X-Y PROJECTION OF THE MOLECULE
SHOWING THERMAL ELLIPSOIDS.

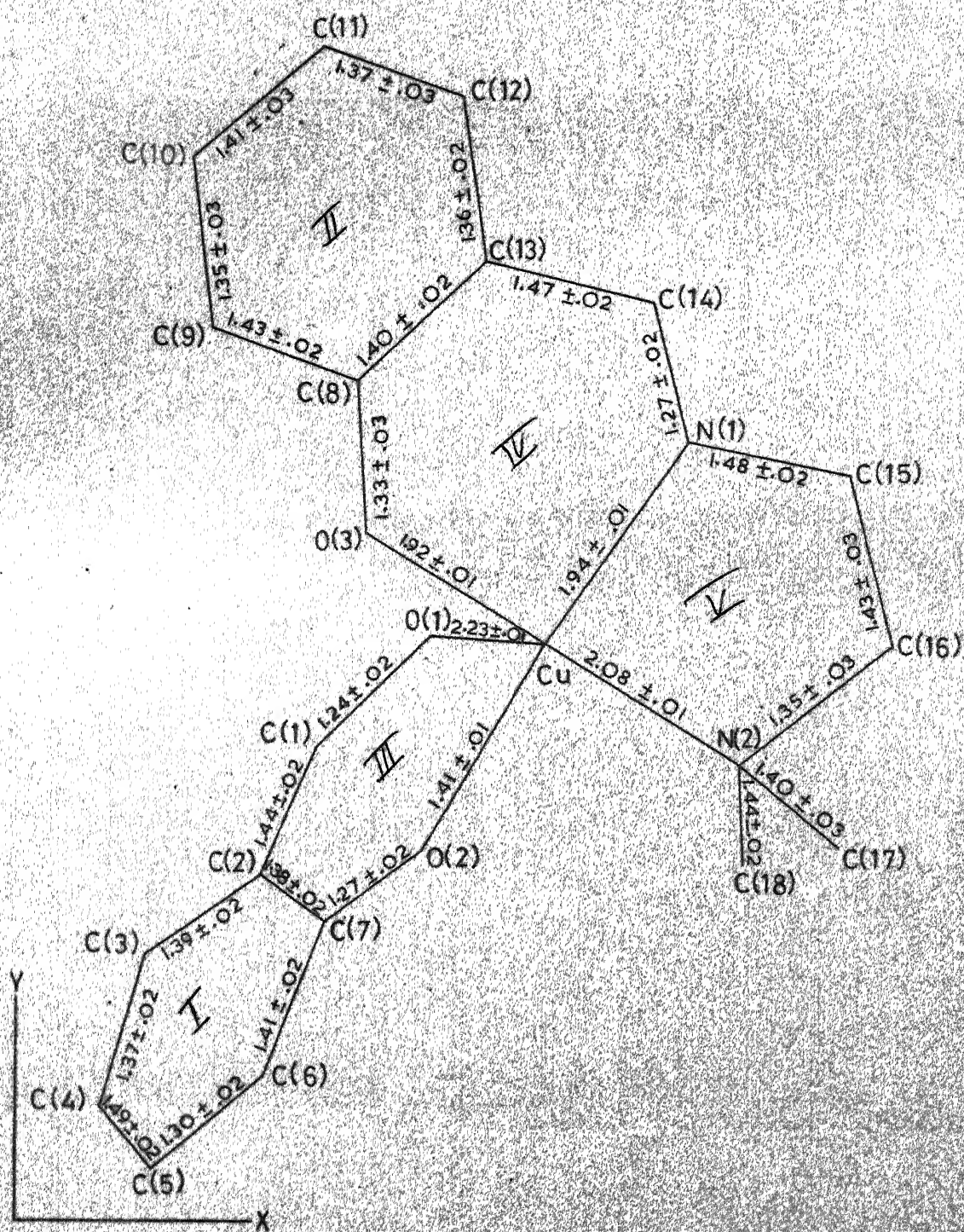


Fig. 4.2a X-Y Projection of the molecule showing the bond-length in Å.

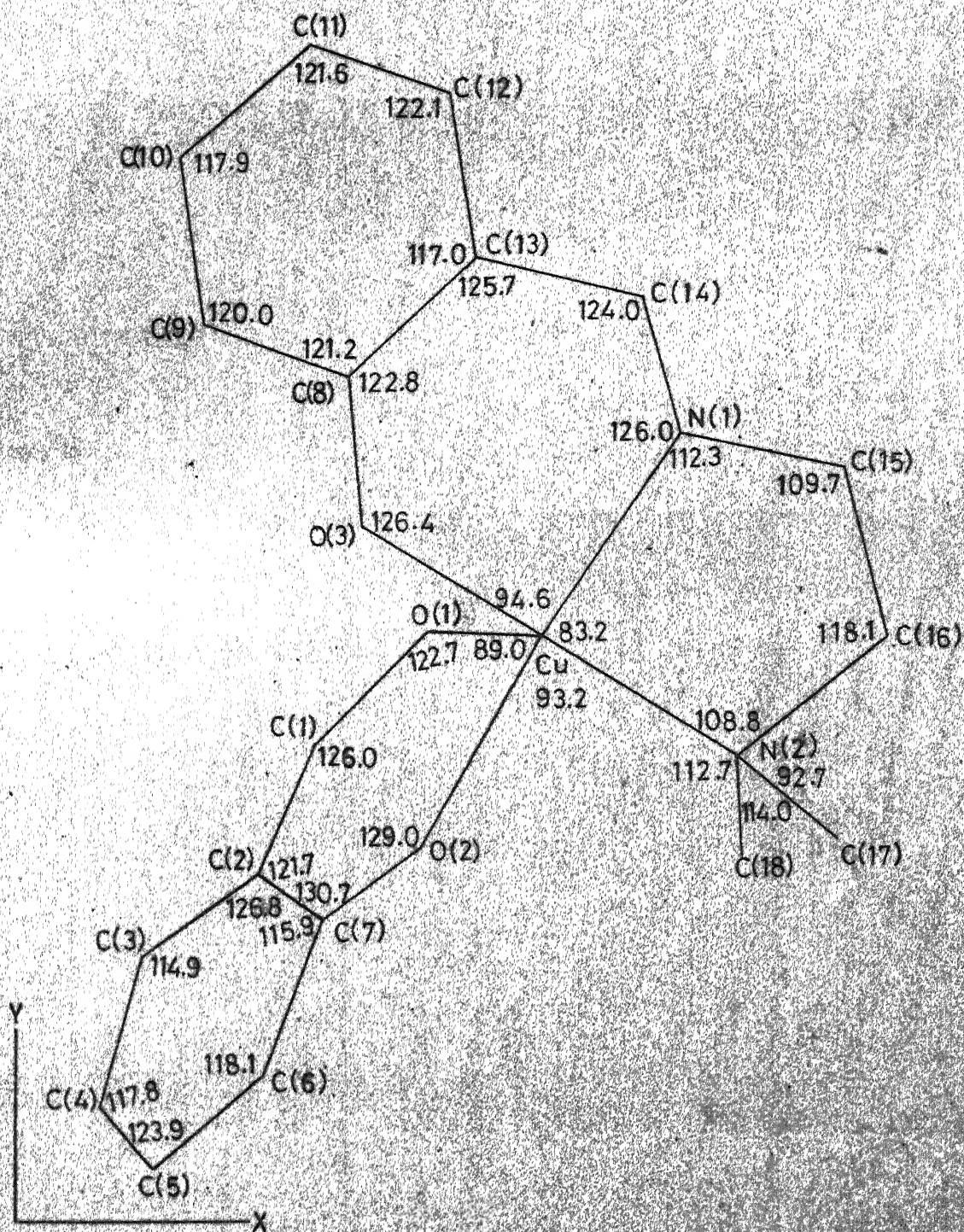


Fig.4.2b X-Y Projection of the molecule showing bond-angles in degrees.

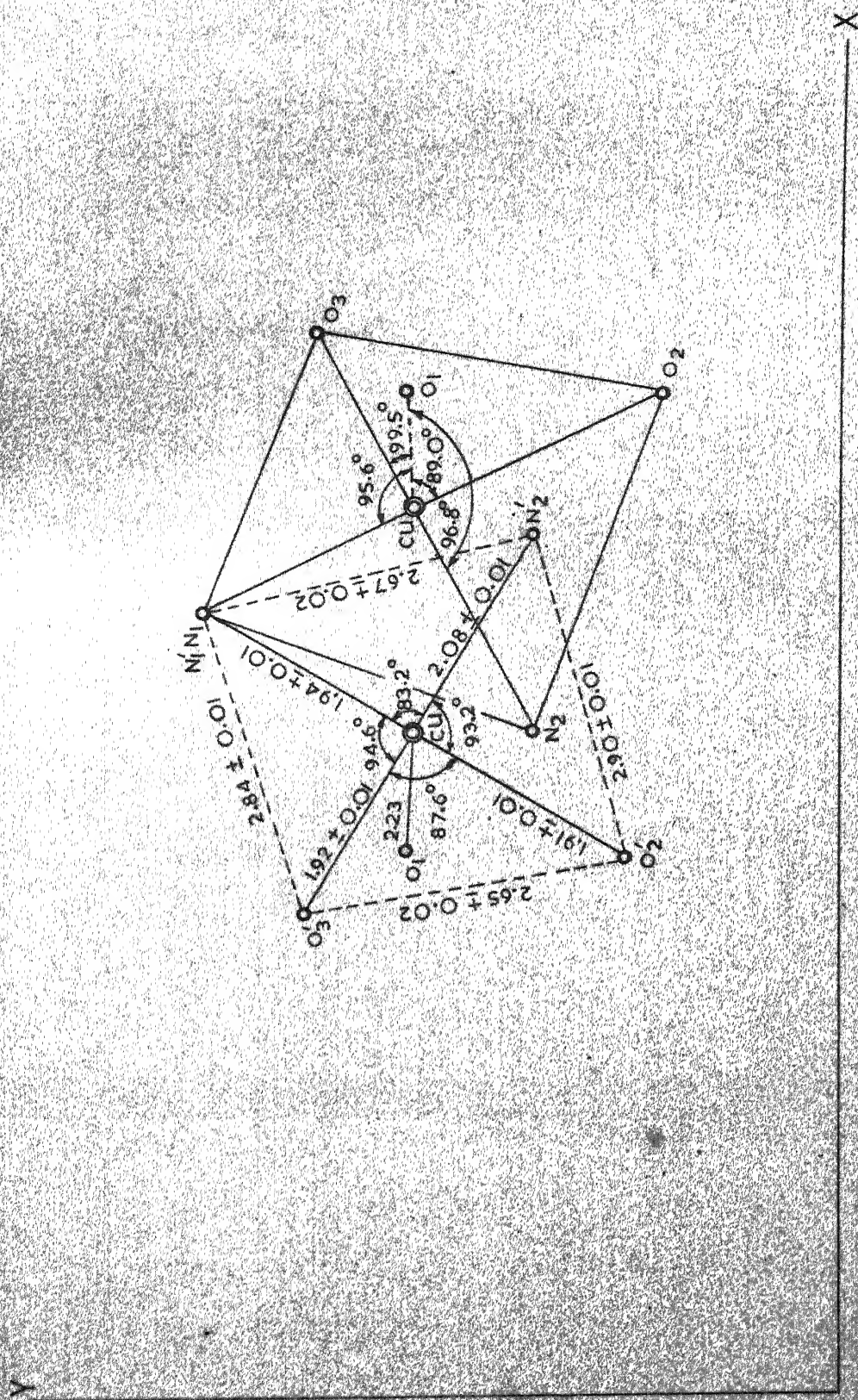


FIG.4.3 X-Y PROJECTION OF THE SQUARE PYRAMID CO-ORDINATION

The average angle around Cu atom in the present structure is 85.0° as compared to 84.5° in $(\text{Cu}(\text{trien})\text{SCN})\text{NCS}^{(33)}$, 85.0° in $\text{Cu}(\text{en}_2)(\text{SCN})_2^{(34)}$, 86.0° in $\text{Cu}(\text{en}_2)(\text{NO}_3)_2^{(35)}$ and 84.1° in $\text{Cu}(\text{tren})\text{NCS}(\text{SCN})^{(36)}$.

The Cu-O(1) bond is almost at right angles to the plane containing Cu, N(1), N(2), O(2) and O(3). The angles of the type O(1)-Cu-N(1), O(1)-Cu-N(2), O(1)-Cu-O(2) and O(1)-Cu-O(3) are shown in Fig. 4.3. Their average is 95.2° . Two parallel sides of the distorted square formed by the atoms O(2) and N(2) and O(3) and N(1) are 2.90 \AA and 2.84 \AA respectively. The other two sides formed by the atoms O(2) and O(3), and N(2) and N(1) are shorter i.e. 2.65 \AA and 2.67 \AA respectively. The equation of the plane forming the base of the square pyramid is

$$0.3985X - 0.2231Y + 0.8896Z = 4.4063 \quad (4.1)$$

Atom N(2) is 0.44 \AA away from this plane while Cu atom is -0.10 \AA away. The deviations of other atoms from this plane are N(1) -0.08 \AA , O(2) 0.03 \AA and O(3) -0.07 \AA .

Cu-N(1) and Cu-N(2) bond lengths are 1.94 \AA and 2.08 \AA . Cu-O(2) and Cu-O(3) bond lengths are 1.91 \AA and 1.92 \AA respectively whereas Cu-O(1) bond length is 2.23 \AA .

The mean bond length of the benzene ring formed by the atoms C(2), C(3), C(4), C(5), C(6) and C(7) is 1.38 \AA and the mean bond angle is 119.5° , while the mean bond length of the benzene ring formed by the atoms C(8), C(9), C(10), C(11), C(12) and C(13) is 1.39 \AA and the mean bond angle is 120.0° .

The equations of the best planes and the deviations of the atoms from them for various rings in the molecule are listed in Table 4.4. These planes are identified in Fig. 4.2a as well as in Table 4.4 by Roman numerals.

Dihedral angle between plane I and plane III is 5.7° , thus they are almost in the same plane. The angle between plane II and plane IV is 4.9° and the angle between plane IV and V is 16.4° . The angle between plane III and plane IV is 81.6° and the angle between plane III and V is 82.7° . Thus the tridentate ligand formed by the rings II, IV and V is at rightangles to the bidentate ligand formed by the rings I and III, which itself is almost planar.

Packing of the molecules in the unit cell is shown in X-Y projection in Fig. 4.4. Anisotropic temperature factors were interpreted in terms of thermal ellipsoids of vibration and are plotted in Fig. 4.1. It is noticed that the amplitude of thermal vibration for the terminal atoms like C(17) and C(18) is much larger as compared to other atoms.

Calculated and observed structure factors are listed in Table 4.5.

TABLE 4.4

I Best Plane Through the Benzene Ring Formed by C(2), C(3), C(4), C(5),
C(6) and C(7)

$$0.7819X - 0.4604Y - 0.4202Z = 3.8693$$

Deviations of constituent atoms from this plane

C(2)	0.0051 Å
C(3)	0.0051 Å
C(4)	0.0051 Å
C(5)	0.0522 Å
C(6)	-0.0319 Å
C(7)	-0.0356 Å

II Best Plane Through the Benzene Ring Formed by the Atoms C(8), C(9),
C(10), C(11), C(12) and C(13)

$$0.4195X - 0.1594Y + 0.8937Z = 4.7331$$

Deviations of constituent atoms from this plane

C(8)	0.0002 Å
C(9)	0.0002 Å
C(10)	0.0002 Å
C(11)	-0.0038 Å
C(12)	-0.0161 Å
C(13)	+0.0194 Å

contd.

III Best Plane Through the Ring Formed by Atoms Cu, O(1), O(2), C(1), C(2), C(7)

$$0.8089X - 0.4864Y - 0.3303Z = 4.0786$$

Deviations of constituent atoms from this plane

Cu	0.0576 Å
O(1)	0.1073 Å
O(2)	0.0290 Å
C(1)	-0.0610 Å
C(2)	-0.0638 Å
C(7)	0.0187 Å

IV Best Plane Through the Ring Formed by Atoms Cu, N(1), O(3), C(8),
C(13), C(14)

$$0.4035X - 0.2431Y + 0.8821Z = 4.1870$$

Deviations of constituent atoms from this plane

Cu	0.0702 Å
N(1)	0.0702 Å
O(3)	0.0702 Å
C(8)	-0.0552 Å
C(13)	-0.1270 Å
C(14)	-0.0285 Å

Contd.

V Best Plane Through the Ring Formed by the Atoms Cu, N(1), N(2),
C(15) and C(16)

$$0.1856X - 0.0866Y + 0.9788Z = 3.2002$$

Deviations of constituent atoms from this plane

Cu	0.0458 Å
N(1)	0.0538 Å
N(2)	0.0409 Å
C(15)	0.1686 Å
C(16)	-0.2109 Å

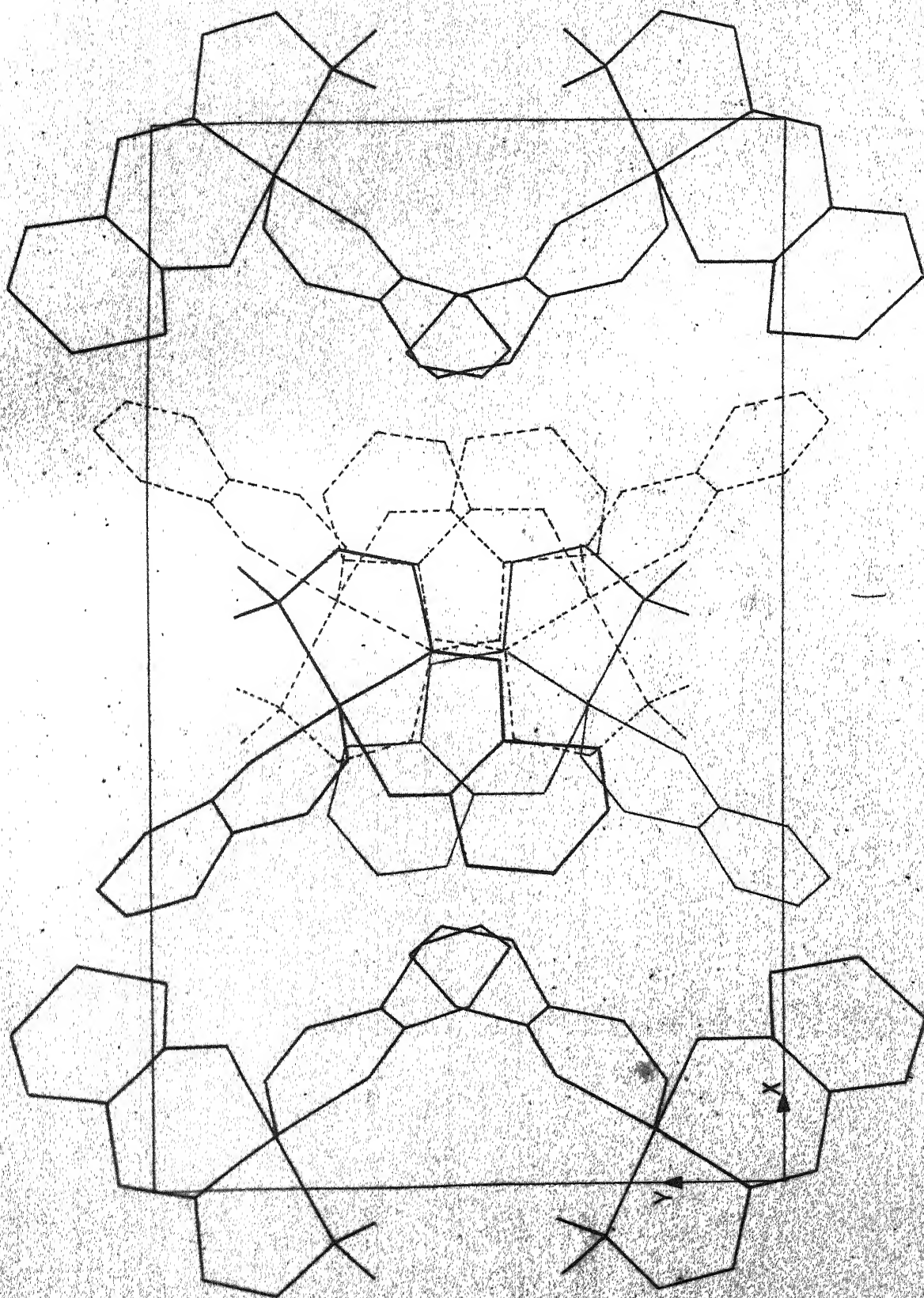


Fig.4.4 X-Y Projection of the molecule showing the packing.

TABLE 4.5

Calculated and Observed Structure Factors for Cu(Sal)(SalNMe₂)
 *indicates unobserved reflections

h	k	l	F ^O	F ^C	h	k	l	F ^O	F ^C
2	0	0	97	106	-16	0	4	6	-8
4	0	0	52	-54	0	0	6	37	37
6	0	0	57	56	2	0	6	14	3
8	0	0	30	-34	-2	0	6	74	70
10	0	0	39	-42	4	0	6	95	-103
12	0	0	18	-23	-4	0	6	27	32
14	0	0	4	-1*	6	0	6	87	94
0	0	2	44	38	-6	0	6	32	40
2	0	2	95	117	8	0	6	3	-5*
-2	0	2	140	-149	-8	0	6	64	68
4	0	2	64	78	10	0	6	14	11
-4	0	2	20	6	-10	0	6	4	3*
6	0	2	2	7	12	0	6	35	37
-6	0	2	44	-46	-12	0	6	12	-11
8	0	2	37	42	14	0	6	4	3*
-8	0	2	33	-36	-14	0	6	27	-34
10	0	2	18	17	16	0	6	22	31
-10	0	2	26	-25	-16	0	6	16	-19
12	0	2	8	-9	0	0	8	96	106
-12	0	2	43	47	2	0	8	41	40
14	0	2	36	-44	-2	0	8	68	73
-14	0	2	20	20	4	0	8	67	72
16	0	2	29	-32	-4	0	8	4	4
-16	0	2	4	7*	6	0	8	11	10
0	0	4	90	-94	-6	0	8	3	1*
2	0	4	286	-294	8	0	8	44	-50
-2	0	4	101	-102	-8	0	8	30	-32
4	0	4	70	-75	10	0	8	23	-25
-4	0	4	36	30	-10	0	8	19	-18
6	0	4	30	37	-12	0	8	19	-21
-6	0	4	3	5*	14	0	8	22	-25
8	0	4	39	46	-14	0	8	19	-24
-8	0	4	26	33	-16	0	8	10	11
10	0	4	27	28	0	0	10	25	19
-10	0	4	48	54	2	0	10	35	36
12	0	4	23	24	-2	0	10	6	9
-12	0	4	22	27	4	0	10	11	12
14	0	4	4	6*	-4	0	10	62	-72
-14	0	4	4	1*	6	0	10	41	39
16	0	4	16	-15	-6	0	10	51	54

table 4.5 contd.

8	0	10	19	12	9	1	1	47	-52
-8	0	10	14	-15	-9	1	1	18	-22
10	0	10	30	13	11	1	1	25	-27
12	0	10	4	9*	-11	1	1	52	-50
-12	0	10	12	12	13	1	1	6	-10
-14	0	10	8	8	-13	1	1	37	-42
0	0	12	28	-26	-15	1	1	14	-13
2	0	12	42	-38	15	1	1	15	15
-2	0	12	38	-40	17	1	1	4	26*
4	0	12	25	-25	-17	1	1	4	-1*
-4	0	12	18	-21	1	1	2	64	-65
6	0	12	7	-10	-1	1	2	60	-65
-6	0	12	23	20	3	1	2	103	109
8	0	12	12	11	-3	1	2	44	39
10	0	12	9	10	5	1	2	7	-6
-10	0	12	25	28	-5	1	2	114	-107
-12	0	12	15	16	7	1	2	17	18
0	0	14	9	-8	-7	1	2	5	-4
2	0	14	20	-22	9	1	2	6	8
-2	0	14	27	26	-9	1	2	33	-25
4	0	14	37	-37	11	1	2	20	19
-4	0	14	41	42	-11	1	2	21	26
6	0	14	17	-16	13	1	2	25	-28
-6	0	14	19	18	-13	1	2	21	23
8	0	14	4	3*	15	1	2	15	-21
-8	0	14	6	6	-15	1	2	13	12
-10	0	14	4	8*	17	1	2	4	-0*
0	0	16	28	30	-17	1	2	4	-2*
2	0	16	19	15	1	1	3	131	138
-2	0	16	12	10	-1	1	3	181	179
-4	0	16	4	-1*	3	1	3	45	54
-6	0	16	6	-8	-3	1	3	17	16
1	1	0	109	108	5	1	3	43	46
3	1	0	57	64	7	1	3	2	-7*
5	1	0	36	-28	-7	1	3	76	-82
7	1	0	5	9	9	1	3	19	-19
9	1	0	19	13	-9	1	3	85	-84
11	1	0	13	10	11	1	3	22	-25
13	1	0	11	-9	-11	1	3	24	-27
15	1	0	26	29	13	1	3	45	-50
17	1	0	4	-1*	-13	1	3	16	17
1	1	1	67	55	15	1	3	24	-29
-1	1	1	176	174	-15	1	3	23	24
3	1	1	32	13	17	1	3	4	-2*
-3	1	1	111	121	-17	1	3	8	8
5	1	1	25	-29	1	1	4	102	-110
7	1	1	38	-42	-1	1	4	23	22
-7	1	1	4	-4	3	1	4	141	-143

table 4.5 contd.

3	1	4	25	-30	1	1	7	110	-115
5	1	4	7	3	-1	1	7	9	-13
-5	1	4	58	56	3	1	7	104	-115
7	1	4	3	2*	-3	1	7	26	32
-7	1	4	23	-15	5	1	7	26	-28
9	1	4	8	10	-5	1	7	47	54
-9	1	4	9	3	7	1	7	9	12
11	1	4	13	12	-7	1	7	49	51
-11	1	4	10	10	9	1	7	36	37
13	1	4	4	-0*	-9	1	7	19	21
-13	1	4	16	-15	11	1	7	28	28
15	1	4	9	-13	-11	1	7	15	14
-15	1	4	4	10*	13	1	7	9	9
17	1	4	17	-19	-13	1	7	4	-2*
-17	1	4	4	-2*	15	1	7	4	16*
1	1	5	101	-97	-15	1	7	11	-12
-1	1	5	78	-89	1	1	8	31	31
3	1	5	56	46	-1	1	8	7	-5
-3	1	5	11	-15	3	1	8	38	41
5	1	5	59	64	-3	1	8	27	26
-5	1	5	58	-54	5	1	8	51	51
7	1	5	53	58	-5	1	8	31	29
-7	1	5	15	-8	7	1	8	14	-19
9	1	5	16	24	-7	1	8	12	-15
-9	1	5	12	9	9	1	8	11	15
11	1	5	13	19	-9	1	8	4	-3*
-11	1	5	48	55	11	1	8	13	-17
13	1	5	9	-8	-11	1	8	4	-2*
-13	1	5	13	13	13	1	8	4	4*
15	1	5	12	-11	-13	1	8	4	-3*
-15	1	5	9	9	15	1	8	7	11
-17	1	5	4	-2*	-15	1	8	4	-4*
1	1	6	63	62	1	1	9	18	22
-1	1	6	30	-26	-1	1	9	52	54
3	1	6	3	1*	3	1	9	4	5
-3	1	6	7	-10	-3	1	9	70	81
5	1	6	42	-44	5	1	9	46	-47
-5	1	6	8	8	-5	1	9	19	27
7	1	6	6	-0	7	1	9	45	-46
-7	1	6	56	54	9	1	9	4	-10*
9	1	6	7	7	-9	1	9	29	-31
-9	1	6	9	4	11	1	9	5	2
-11	1	6	22	-33	-11	1	9	13	-9
13	1	6	12	18	13	1	9	4	-9*
-13	1	6	9	-18	-13	1	9	20	-20
15	1	6	4	11*	-15	1	9	14	-17
-15	1	6	4	-4*	1	1	10	15	13
-17	1	6	6	-9	-1	1	10	4	0*

table 4.5 contd.

3	1	10	13	-11	1	1	14	6	-5
-3	1	10	13	12	-1	1	14	4	-1*
5	1	10	4	-1	3	1	14	5	-4
7	1	10	7	3	-3	1	14	18	22
-7	1	10	24	-23	5	1	14	9	7
9	1	10	18	19	-5	1	14	4	4*
-9	1	10	9	10	7	1	14	4	-1*
11	1	10	10	-10*	-7	1	14	6	4
-11	1	10	4	1*	-9	1	14	4	1*
13	1	10	7	-10	1	1	15	25	-20
-13	1	10	11	15	-1	1	15	4	-2*
-15	1	10	4	2*	3	1	15	34	-33
1	1	11	35	37	-3	1	15	12	9
-1	1	11	29	27	5	1	15	14	-14
3	1	11	47	51	-5	1	15	20	19
-3	1	11	7	-6	-7	1	15	11	14
5	1	11	59	59	1	1	16	8	7
-5	1	11	34	-34	-1	1	16	17	17
7	1	11	4	-4*	3	1	16	4	1*
-7	1	11	36	-36	-3	1	16	4	-5*
9	1	11	16	-19	-5	1	16	4	-5*
-9	1	11	17	-17	0	2	0	75	-67
11	1	11	20	-21	2	2	0	135	-126
-11	1	11	6	9	4	2	0	79	66
-13	1	11	4	-1*	6	2	0	55	57
1	1	12	5	-8	8	2	0	70	70
-1	1	12	18	-16	10	2	0	56	58
-3	1	12	20	-23	12	2	0	34	42
5	1	12	4	2	14	2	0	21	23
-5	1	12	12	-14	0	2	1	29	-13
7	1	12	21	-26	2	2	1	24	29
-7	1	12	6	5	-2	2	1	15	26
9	1	12	4	17*	4	2	1	49	-41
-9	1	12	5	5	-4	2	1	78	81
11	1	12	4	5*	6	2	1	36	-41
-11	1	12	4	8	-6	2	1	65	59
-13	1	12	6	7	8	2	1	7	-18
1	1	13	17	-12	10	2	1	50	-48
-1	1	13	26	-22	-10	2	1	12	-17
3	1	13	4	-1*	12	2	1	8	-7
-3	1	13	18	-19	-12	2	1	30	-34
5	1	13	19	17	14	2	1	26	28
-5	1	13	11	-12	-14	2	1	28	-29
7	1	13	26	22	16	2	1	24	27
-7	1	13	4	-3	-16	2	1	4	-3*
9	1	13	16	17	0	2	2	23	-17
-9	1	13	4	0	2	2	2	41	-41
-11	1	13	13	13	-2	2	2	53	-41

table 4.5 contd.

4	2	2	53	-48	2	2	5	30	-35
-4	2	2	129	119	-2	2	5	7	-3
6	2	2	79	-74	4	2	5	9	-3
-6	2	2	41	42	-4	2	5	11	-15
8	2	2	3	-2	6	2	5	27	32
-8	2	2	18	19	-6	2	5	107	-99
10	2	2	9	-9	8	2	5	33	39
-10	2	2	9	-12	-8	2	5	10	-6
12	2	2	21	22	10	2	5	10	18
-12	2	2	7	-3	-10	2	5	61	59
14	2	2	19	16	12	2	5	8	6
-14	2	2	22	-18	-12	2	5	35	37
16	2	2	12	14	14	2	5	4	-9*
-15	2	2	16	-14	-14	2	5	14	16
0	2	3	83	77	16	2	5	20	-27
2	2	3	6	10	-16	2	5	4	6
-2	2	3	23	-10	0	2	6	14	-9
4	2	3	25	24	2	2	6	52	59
-4	2	3	67	64	-2	2	6	39	-36
-6	2	3	61	-56	4	2	6	74	80
8	2	3	9	10	-4	2	6	32	-34
-8	2	3	89	-80	6	2	6	37	41
-10	2	3	6	6	-6	2	6	32	-42
10	2	3	4	1*	8	2	6	33	34
12	2	3	33	-38	-8	2	6	14	-14
-12	2	3	25	21	10	2	6	13	-10
14	2	3	16	-19	-10	2	6	23	-27
-14	2	3	32	30	12	2	6	4	-19*
-16	2	3	11	10	-12	2	6	17	17
16	2	3	7	-11	14	2	6	21	-24
0	2	4	40	43	-14	2	6	24	22
2	2	4	35	39	-16	2	6	10	7
-2	2	4	10	21	0	2	7	21	-23
4	2	4	51	44	2	2	7	84	-90
-4	2	4	55	50	-2	2	7	36	-40
6	2	4	60	-66	4	2	7	58	-61
-6	2	4	78	-68	6	2	7	5	-0
8	2	4	33	-43	-6	2	7	31	35
-8	2	4	73	-69	8	2	7	22	20
10	2	4	51	-56	-8	2	7	39	43
-10	2	4	44	-45	10	2	7	19	18
12	2	4	45	-49	-10	2	7	7	6
-12	2	4	42	-46	12	2	7	6	6
14	2	4	14	-15	-12	2	7	31	32
-14	2	4	18	-18	14	2	7	17	19
16	2	4	4	6*	-14	2	7	4	3*
-16	2	4	17	20	-16	2	7	4	-1*
0	2	5	26	-28	0	2	8	63	-68

table 4.5 contd.

2	2	8	35	-41	8	2	11	8	8
-2	2	8	37	-42	-8	2	11	37	-29
4	2	8	31	23	10	2	11	17	-18
-4	2	8	10	8	-10	2	11	6	10
6	2	8	9	16	12	2	11	16	-17
-6	2	8	47	47	-12	2	11	7	7
8	2	8	28	34	0	2	12	25	26
-8	2	8	30	28	2	2	12	38	35
10	2	8	28	32	-2	2	12	5	8
-10	2	8	41	40	4	2	12	6	8
12	2	8	27	30	-4	2	12	4	1*
-12	2	8	31	30	6	2	12	26	-22
14	2	8	9	9	-6	2	12	9	7
-14	2	8	5	-9	8	2	12	10	-9
-16	2	8	7	-5	-8	2	12	36	-36
0	2	9	3	-2*	10	2	12	16	-22
2	2	9	19	20	-10	2	12	20	-18
-2	2	9	20	24	-12	2	12	4	-3*
4	2	9	22	-25	0	2	13	20	-25
-4	2	9	42	47	2	2	13	4	8*
6	2	9	24	-25	-2	2	13	14	-19
-6	2	9	18	-21	4	2	13	8	-10
8	2	9	14	-19	-4	2	13	16	-19
-8	2	9	13	14	6	2	13	9	8
10	2	9	18	-20	-6	2	13	7	-7
-10	2	9	28	-28	8	2	13	33	33
12	2	9	4	1*	-8	2	13	4	-2*
-12	2	9	14	-12	-10	2	13	13	15
14	2	9	4	13*	0	2	14	4	-1*
-14	2	9	4	0*	2	2	14	17	17
0	2	10	5	-4	-2	2	14	13	-14
2	2	10	35	-37	4	2	14	27	28
4	2	10	56	-58	-4	2	14	18	-18
6	2	10	20	-23	6	2	14	19	27
-6	2	10	36	40	-6	2	14	19	-19
8	2	10	4	-6	8	2	14	13	11
-8	2	10	17	18	-8	2	14	5	-4
10	2	10	12	-15	-10	2	14	4	-8*
-10	2	10	5	-8	2	2	15	10	-6
12	2	10	17	16	-2	2	15	4	-4*
-12	2	10	9	-8	-4	2	15	4	5*
-14	2	10	8	-7	-6	2	15	4	0*
2	2	11	15	19	-8	2	15	4	-4*
-2	2	11	4	9*	0	2	16	13	-10
4	2	11	18	17	2	2	16	13	-14
-4	2	11	4	-6*	-2	2	16	7	-8
6	2	11	21	24	-4	2	16	4	-1*
-6	2	11	23	-24	1	3	0	45	-44

table 4.5 contd.

3	3	0	2	4*	9	3	3	28	32
5	3	0	35	30	-9	3	3	10	12
7	3	0	49	53	11	3	3	40	41
9	3	0	32	39	-11	3	3	27	23
11	3	0	31	38	13	3	3	18	20
13	3	0	12	13	-13	3	3	9	11
15	3	0	4	6*	15	3	3	11	12
1	3	1	20	-5	-15	3	3	4	6*
-1	3	1	43	-43	-17	3	3	14	-18
3	3	1	11	-14	1	3	4	34	35
-3	3	1	88	-83	-1	3	4	12	23
5	3	1	32	34	3	3	4	24	22
7	3	1	84	81	-3	3	4	5	7
-7	3	1	49	47	5	3	4	31	23
9	3	1	22	31	-5	3	4	44	39
-9	3	1	25	24	7	3	4	38	-44
11	3	1	10	11	-7	3	4	10	4
-11	3	1	20	25	9	3	4	83	-81
13	3	1	13	13	-9	3	4	76	-69
-13	3	1	15	16	11	3	4	40	-47
15	3	1	4	2*	-11	3	4	32	-30
-15	3	1	7	4	13	3	4	4	-17*
17	3	1	4	-7*	-13	3	4	21	-24
-17	3	1	4	-8*	15	3	4	4	6*
1	3	2	29	-24	-15	3	4	4	0*
-1	3	2	32	30	-17	3	4	4	12*
3	3	2	70	-64	1	3	5	39	40
-3	3	2	75	69	-1	3	5	57	55
5	3	2	61	-60	3	3	5	7	9
-5	3	2	106	104	-3	3	5	40	36
-7	3	2	98	92	5	3	5	35	-35
-7	3	2	60	-70	-5	3	5	7	-5
9	3	2	41	-42	-7	3	5	39	32
-9	3	2	4	-5*	7	3	5	7	-14
11	3	2	17	13	9	3	5	46	-48
-11	3	2	32	-36	-9	3	5	50	52
13	3	2	25	29	11	3	5	14	-14
-13	3	2	30	-27	-11	3	5	13	-10
15	3	2	21	25	13	3	5	4	4*
-15	3	2	26	-24	-13	3	5	9	-5
-17	3	2	8	-8	15	3	5	4	6*
1	3	3	7	-16	-15	3	5	10	-7
-1	3	3	43	-44	1	3	6	34	28
3	3	3	34	-37	-1	3	6	29	-27
-3	3	3	2	-9	3	3	6	9	14
5	3	3	69	-62	-3	3	6	19	-23
7	3	3	22	-15	5	3	6	67	70
-7	3	3	91	76	-5	3	6	22	-30

table 4.5 contd.

7	3	6	58	64	9	3	9	11	13
-7	3	6	55	-57	-9	3	9	5	-5
9	3	6	4	10*	11	3	9	15	12
-9	3	6	23	-23	-11	3	9	14	9
11	3	6	13	-13	13	3	9	4	0*
-11	3	6	26	28	-13	3	9	10	10
13	3	6	17	-20	15	3	9	4	1*
-13	3	6	32	28	1	3	10	8	-10
15	3	6	4	-22*	-1	3	10	15	-10
-15	3	6	15	13	3	3	10	28	-34
1	3	7	47	49	-3	3	10	25	-31
-1	3	7	10	13	5	3	10	15	-21
3	3	7	49	41	-5	3	10	46	51
-3	3	7	32	-33	7	3	10	33	-33
5	3	7	19	19	-7	3	10	41	43
-5	3	7	23	-24	9	3	10	23	-26
7	3	7	16	13	-9	3	10	4	4*
-7	3	7	20	-21	11	3	10	4	-3
9	3	7	4	-5*	-11	3	10	26	-28
-9	3	7	48	-54	-13	3	10	16	-11
11	3	7	31	-31	1	3	11	11	-16
-11	3	7	17	-15	-1	3	11	4	2*
13	3	7	28	-28	3	3	11	22	-24
-13	3	7	4	-16*	-3	3	11	4	4
15	3	7	4	-5	5	3	11	4	4*
-15	3	7	5	5	-5	3	11	14	14
1	3	8	26	-33	7	3	11	14	-15
-1	3	8	39	-43	-7	3	11	34	33
3	3	8	10	-18	9	3	11	4	3*
-3	3	8	20	-18	-9	3	11	40	37
5	3	8	12	9	11	3	11	9	11
-5	3	8	4	4*	-11	3	11	10	14
7	3	8	24	24	-13	3	11	4	-7*
-7	3	8	26	29	1	3	12	15	14
9	3	8	29	34	-1	3	12	28	28
-9	3	8	39	37	3	3	12	6	5
11	3	8	23	28	-3	3	12	25	24
-11	3	8	31	34	5	3	12	4	2*
13	3	8	18	20	-5	3	12	4	10*
-13	3	8	4	-6*	7	3	12	16	-20
15	3	8	4	4*	-7	3	12	16	-12
1	3	9	15	-15	9	3	12	4	-25*
-1	3	9	24	-26	-9	3	12	34	-35
3	3	9	5	7	-11	3	12	6	-4
-3	3	9	15	-18	1	3	13	13	9
5	3	9	12	15	-1	3	13	17	20
7	3	9	14	16	3	3	13	12	-15
-7	3	9	10	10	-3	3	13	7	9

table 4.5 contd.

5	3	13	4	2*	-2	4	2	12	9
-5	3	13	4	2	4	4	2	16	9
7	3	13	10	-14	-4	4	2	17	-11
-7	3	13	16	20	6	4	2	24	22
-9	3	13	4	1*	8	4	2	36	31
-1	3	14	4	-12*	-8	4	2	15	2
3	3	14	4	-0*	10	4	2	11	-19
-3	3	14	15	-20	-10	4	2	8	18
5	3	14	21	23	12	4	2	4	-6*
-5	3	14	4	-13*	-12	4	2	4	2*
7	3	14	19	21	14	4	2	4	-7*
-7	3	14	12	-9	-14	4	2	4	5*
-9	3	14	4	2*	16	4	2	4	-1*
1	3	15	14	13	-16	4	2	9	8
-1	3	15	6	10	0	4	3	32	-24
3	3	15	4	-1*	2	4	3	50	-45
-3	3	15	9	-8	-2	4	3	33	-25
-5	3	15	15	-14	4	4	3	36	-32
-7	3	15	12	-16	-4	4	3	64	65
-1	3	16	23	-24	6	4	3	71	-71
0	4	0	13	14	-6	4	3	89	73
2	4	0	17	19	8	4	3	24	-26
4	4	0	28	33	-8	4	3	64	56
6	4	0	36	22	10	4	3	40	44
8	4	0	16	-20	-10	4	3	35	29
10	4	0	30	-38	12	4	3	36	41
12	4	0	4	-3*	-12	4	3	7	-9
14	4	0	6	-3	14	4	3	15	26
16	4	0	5	9	-14	4	3	9	-12
0	4	1	15	-19	16	4	3	4	-3*
2	4	1	13	21	-16	4	3	10	-8
-2	4	1	119	-105	0	4	4	17	-23
4	4	1	72	70	2	4	4	50	-42
-4	4	1	113	-112	-2	4	4	13	-22
6	4	1	75	72	4	4	4	28	-25
-6	4	1	63	-55	-4	4	4	62	-56
8	4	1	66	70	6	4	4	30	-18
-8	4	1	20	10	-6	4	4	14	-8
10	4	1	36	42	8	4	4	18	25
-10	4	1	38	31	-8	4	4	57	48
12	4	1	5	8	10	4	4	10	13
-12	4	1	32	38	-10	4	4	8	11
14	4	1	12	-11	12	4	4	20	20
-14	4	1	18	16	-12	4	4	4	0*
16	4	1	15	-17	14	4	4	11	6
-16	4	1	4	-3*	-14	4	4	9	15
0	4	2	18	-7	-16	4	4	4	2*
2	4	2	16	-0	0	4	5	67	69

table 4.5 contd.

2	4	5	4	6	4	4	8	32	29
-2	4	5	60	60	-4	4	8	17	-20
4	4	5	6	-18	6	4	8	10	13
-4	4	5	82	76	-6	4	8	14	-16
6	4	5	63	-65	8	4	8	4	-1*
-6	4	5	28	28	-8	4	8	8	-8
8	4	5	81	-81	10	4	8	12	-13
-8	4	5	9	14	-10	4	8	21	-26
10	4	5	28	-34	12	4	8	9	-9
-10	4	5	32	-30	-12	4	8	4	-4*
12	4	5	4	-0*	-14	4	8	4	7*
-12	4	5	46	-46	0	4	9	34	-34
14	4	5	16	20	2	4	9	8	-8
-14	4	5	13	-14	4	4	9	23	19
-16	4	5	5	-7	-4	4	9	49	-51
0	4	6	26	-23	6	4	9	43	47
2	4	6	22	-20	-6	4	9	16	-17
-2	4	6	5	-3	8	4	9	34	33
4	4	6	22	15	-8	4	9	12	13
-4	4	6	21	18	10	4	9	24	27
6	4	6	22	-19	-10	4	9	15	13
-6	4	6	3	1*	12	4	9	4	5*
8	4	6	5	-5	-12	4	9	19	16
-8	4	6	29	30	-14	4	9	16	21
10	4	6	4	4*	0	4	10	9	7
-10	4	6	7	-12	2	4	10	12	15
12	4	6	7	15	-2	4	10	15	-18
-12	4	6	8	-9	4	4	10	8	12
14	4	6	9	14	-4	4	10	4	-0*
-14	4	6	7	12	6	4	10	6	6
0	4	7	26	29	-6	4	10	22	-26
2	4	7	39	44	8	4	10	8	10
-2	4	7	16	-18	-8	4	10	16	-12
4	4	7	54	55	-10	4	10	7	-6
-4	4	7	44	-40	12	4	10	8	-12
6	4	7	21	23	-12	4	10	4	-1*
-6	4	7	47	-46	0	4	11	19	-13
8	4	7	7	-11	2	4	11	4	-4*
-8	4	7	36	-32	-2	4	11	9	-7
10	4	7	16	-17	4	4	11	17	-18
-10	4	7	27	-23	-4	4	11	4	1*
12	4	7	29	-30	6	4	11	19	-15
-12	4	7	20	-20	-6	4	11	42	44
14	4	7	10	-10	8	4	11	4	-1*
-14	4	7	5	5	-8	4	11	35	30
0	4	8	30	34	10	4	11	9	15
2	4	8	7	-6	-10	4	11	23	24
-2	4	8	31	32	-12	4	11	4	5*

table 4.5 contd.

0	4	12	22	-25	-11	5	1	4	-6*
2	4	12	10	-10	13	5	1	12	23
-2	4	12	4	5*	-13	5	1	11	-18
4	4	12	8	13	15	5	1	4	1*
-4	4	12	4	3*	-15	5	1	4	6*
6	4	12	8	-10	1	5	2	47	39
-6	4	12	5	-8	-1	5	2	17	-22
8	4	12	4	-0*	3	5	2	66	66
-8	4	12	9	9	-3	5	2	89	-79
-10	4	12	10	11	5	5	2	78	81
0	4	13	18	15	-5	5	2	86	-91
2	4	13	19	18	7	5	2	51	52
-2	4	13	20	26	-7	5	2	73	-63
4	4	13	4	-7*	9	5	2	30	37
-4	4	13	20	25	-9	5	2	4	-6*
6	4	13	4	-20*	11	5	2	13	-17
-6	4	13	17	21	-11	5	2	14	19
8	4	13	25	-27	13	5	2	24	-23
-8	4	13	4	-5*	-13	5	2	33	35
-10	4	13	12	-13	15	5	2	18	-23
0	4	14	4	-4*	-15	5	2	9	8
2	4	14	4	-5*	1	5	3	13	-11
-2	4	14	4	12*	-1	5	3	23	19
-4	4	14	9	9	3	5	3	12	-11
6	4	14	4	-5*	-5	5	3	3	-9*
-6	4	14	4	-7*	7	5	3	13	4
-8	4	14	13	16	-7	5	3	18	11
0	4	15	8	8	9	5	3	12	-19
2	4	15	12	15	-9	5	3	7	2
-2	4	15	9	11	11	5	3	6	-11
-4	4	15	15	-12	-11	5	3	11	17
1	5	0	82	90	13	5	3	4	2*
3	5	0	7	8	-13	5	3	6	-9
5	5	0	11	-9	15	5	3	4	-2*
7	5	0	43	-37	-15	5	3	13	13
9	5	0	26	-30	1	5	4	28	-25
11	5	0	33	-41	-1	5	4	30	-39
13	5	0	10	-13	3	5	4	58	-46
15	5	0	4	-3*	-3	5	4	72	-65
1	5	1	8	6	5	5	4	9	2
3	5	1	54	44	-5	5	4	7	-3
-3	5	1	10	8	7	5	4	27	27
5	5	1	36	30	-7	5	4	25	21
-5	5	1	13	13	9	5	4	40	50
7	5	1	11	-17	-9	5	4	30	27
9	5	1	7	-13	11	5	4	36	42
-9	5	1	6	7	13	5	4	4	7*
11	5	1	4	5*	-13	5	4	23	20

table 4.5 contd.

15	5	4	7	-5	7	5	8	23	-26
-15	5	4	9	-10	-7	5	8	25	-26
1	5	5	22	15	9	5	8	28	-37
-1	5	5	3	2*	-9	5	8	27	26
3	5	5	11	-12	-11	5	8	15	-16
-3	5	5	28	21	-13	5	8	19	-26
5	5	5	45	-34	1	5	9	5	-6
-5	5	5	17	-14	-1	5	9	24	-34
-9	5	5	7	14	3	5	9	8	2
11	5	5	9	5	-3	5	9	6	6
-11	5	5	12	15	5	5	9	9	6
13	5	5	4	-4*	-5	5	9	6	0
-13	5	5	4	-5*	7	5	9	4	2*
1	5	6	9	8	-7	5	9	7	-12
-1	5	6	15	15	9	5	9	4	1*
3	5	6	38	-40	-9	5	9	6	8
-3	5	6	61	71	11	5	9	4	-4*
5	5	6	86	-81	-11	5	9	4	3
-5	5	6	76	69	-13	5	9	9	-8
7	5	6	52	-56	1	5	10	12	13
-7	5	6	23	25	-1	5	10	14	-16
9	5	6	14	-20	3	5	10	20	26
-9	5	6	11	9	-3	5	10	41	-41
11	5	6	17	21	5	5	10	21	24
11	5	6	4	2*	-5	5	10	51	-51
13	5	6	16	19	7	5	10	36	34
-13	5	6	24	-32	-7	5	10	20	-15
-15	5	6	22	-25	9	5	10	16	12
1	5	7	23	-22	-9	5	10	4	2*
-1	5	7	42	-41	11	5	10	4	-0*
3	5	7	9	5	-11	5	10	10	10
-3	5	7	15	-12	1	5	11	8	10
5	5	7	13	-8	-1	5	11	4	-3*
-5	5	7	6	-2	3	5	11	13	14
7	5	7	9	-12	-3	5	11	4	4*
-7	5	7	15	-15	5	5	11	5	3
9	5	7	5	-0	-5	5	11	4	-4*
-9	5	7	5	-4*	7	5	11	6	2
11	5	7	8	13	-7	5	11	4	0*
-11	5	7	4	8*	9	5	11	8	11
13	5	7	7	12	-9	5	11	7	5
-13	5	7	17	-19	-11	5	11	10	10
1	5	8	39	39	1	5	12	35	-35
-1	5	8	69	71	-1	5	12	28	-25
3	5	8	4	13	3	5	12	14	-19
-3	5	8	44	46	-3	5	12	27	29
5	5	8	15	-15	5	5	12	9	7
-5	5	8	11	-11	-5	5	12	4	-1*

table 4.5 contd.

7	5	12	18	20	12	6	2	9	17
-7	5	12	26	26	-12	6	2	8	8
-9	5	12	13	12	14	6	2	14	-16
1	5	12	9	8	-14	6	2	8	-10
-1	5	13	4	-15*	2	6	3	34	32
-3	5	13	4	5*	-2	6	3	44	31
5	5	13	4	-0*	4	6	3	20	30
-5	5	13	4	3*	-4	6	3	58	-50
-7	5	13	5	-10	6	6	3	37	42
1	5	14	8	11	-6	6	3	53	-50
-1	5	14	10	13	8	6	3	4	3*
3	5	14	20	-23	-8	6	3	4	-4*
-3	5	14	11	13	-10	6	3	15	-17
-5	5	14	20	20	10	6	3	4	-0*
3	5	15	4	-2*	12	6	3	23	-31
0	6	0	26	26	-12	6	3	11	12
2	6	0	11	15	14	6	3	16	-23
4	6	0	32	-23	-14	6	3	16	16
6	6	0	22	-21	0	6	4	3	-6*
8	6	0	14	-14	2	6	4	4	-2*
10	6	0	8	5	-2	6	4	3	-2*
12	6	0	4	-10*	4	6	4	19	16
14	6	0	22	-30	-4	6	4	3	-0*
0	6	1	43	36	6	6	4	17	9
2	6	1	11	12	-6	6	4	16	-10
-2	6	1	83	71	8	6	4	10	13
4	6	1	11	-21	-8	6	4	4	12*
-4	6	1	67	56	10	6	4	4	5*
6	6	1	55	-54	-10	6	4	24	31
-6	6	1	27	21	12	6	4	4	9*
8	6	1	43	-47	-12	6	4	7	6
-8	6	1	11	-2	14	6	4	4	10*
10	6	1	4	-10*	-14	6	4	6	-4
-10	6	1	33	-28	0	6	5	33	-34
12	6	1	4	4*	2	6	5	11	12
-12	6	1	20	-23	-2	6	5	78	-72
14	6	1	4	14*	4	6	5	32	35
-14	6	1	12	-17	-4	6	5	52	49
0	6	2	29	-32	6	6	5	43	52
-2	6	2	15	-13	-6	6	5	21	-24
4	6	2	22	25	8	6	5	45	51
-4	6	2	35	-22	-8	6	5	4	-1*
6	6	2	8	6	10	6	5	23	25
-6	6	2	23	-15	-10	6	5	21	15
8	6	2	4	1*	12	6	5	6	-10
-8	6	2	9	-10	-12	6	5	26	30
10	6	2	6	1	-14	6	5	27	29
-10	6	2	4	2	0	6	6	27	24

table 4.5 contd.

2	6	6	8	-9	-10	6	9	14	-17
-2	6	6	22	23	-12	6	9	22	-24
4	6	6	31	-38	0	6	10	11	7
-4	6	6	9	12	-2	6	10	20	-20
6	6	6	26	-32	4	6	10	4	1*
-6	6	6	12	11	-4	6	10	4	-5*
8	6	6	8	5	6	6	10	4	9
-8	6	6	10	14	-6	6	10	4	-3*
10	6	6	9	3	8	6	10	4	8*
-10	6	6	7	-10	-8	6	10	4	1*
12	6	6	4	-4*	-10	6	10	4	2*
-12	6	6	4	5*	0	6	11	24	27
-14	6	6	4	-2*	2	6	11	4	3*
0	6	7	42	-43	-2	6	11	14	15
2	6	7	61	-62	4	6	11	27	31
-2	6	7	11	11	-4	6	11	19	-21
4	6	7	27	-31	6	6	11	14	15
-4	6	7	28	27	-6	6	11	5	0*
6	6	7	8	-11	8	6	11	6	-10
-6	6	7	29	35	-8	6	11	4	-12*
8	6	7	4	5*	-10	6	11	9	-12
-8	6	7	6	4	0	6	12	11	-12
10	6	7	19	22	2	6	12	4	-6
-10	6	7	4	-1*	-2	6	12	12	-17
12	6	7	10	11	-4	6	12	16	15
-12	6	7	4	4*	6	6	12	6	4
0	6	8	38	38	-6	6	12	8	7
2	6	8	4	0*	-8	6	12	4	1
-2	6	8	4	-0*	0	6	13	18	-22
4	6	8	16	-14	2	6	13	14	-12
-4	6	8	11	13	-2	6	13	19	-20
6	6	8	23	-28	4	6	13	7	8
-6	6	8	4	-3	-4	6	13	8	-13
8	6	8	11	-12	-6	6	13	4	-6*
-8	6	8	23	-22	0	6	14	4	5*
10	6	8	4	3*	2	6	14	11	11
-10	6	8	9	-9	3	7	0	46	-39
-12	6	8	4	7*	5	7	0	19	20
0	6	9	40	43	7	7	0	16	17
2	6	9	6	-1	9	7	0	30	29
-2	6	9	56	64	11	7	00	4	-10
4	6	9	29	-29	13	7	0	4	3*
-4	6	9	36	36	1	7	1	26	22
6	6	9	35	-35	-1	7	1	4	10*
-6	6	9	4	5	3	7	1	10	-12
8	6	9	31	-37	-3	7	1	55	48
-8	6	9	8	-8	5	7	1	36	-34
10	6	9	4	-3*	-5	7	1	22	29

table 4.5 contd.

7	7	1	18	-17	-1	7	5	21	-29
-7	7	1	6	-8	3	7	5	4	-2
9	7	1	4	2*	-3	7	5	4	-2*
-9	7	1	24	-26	5	7	5	27	30
11	7	1	17	-18	-5	7	5	23	-22
-11	7	1	4	-6*	7	7	5	24	27
13	7	1	5	3	-7	7	5	4	6*
-13	7	1	10	-8	9	7	5	12	19
1	7	2	29	-25	-9	7	5	13	9
-1	7	2	19	16	11	7	5	4	-1*
3	7	2	32	-40	-11	7	5	10	10
-3	7	2	51	51	-13	7	5	15	15
5	7	2	48	-53	-1	7	6	24	-34
-5	7	2	47	48	3	7	6	24	27
7	7	2	41	-43	-3	7	6	40	-46
-7	7	2	26	33	5	7	6	23	29
9	7	2	4	4*	-5	7	6	36	-42
-9	7	2	4	3*	7	7	6	35	40
11	7	2	4	8*	-7	7	6	4	-11*
-11	7	2	20	-20	9	7	6	11	10
13	7	2	13	19	-9	7	6	5	-9
-13	7	2	4	0*	11	7	6	4	-4*
1	7	3	28	31	-11	7	6	4	4*
-1	7	3	18	19	1	7	7	29	-29
3	7	3	12	18	-1	7	7	9	-9
-3	7	3	11	16	3	7	7	43	-49
5	7	3	19	20	-3	7	7	4	8*
-5	7	3	20	-19	5	7	7	4	-7*
7	7	3	6	-0	-5	7	7	4	7*
-7	7	3	19	-29	7	7	7	9	5
9	7	3	4	6*	-7	7	7	4	10
-9	7	3	16	15	9	7	7	13	11
11	7	3	14	-20	-9	7	7	4	-1*
-11	7	3	7	8	11	7	7	7	4
13	7	3	15	-21	-11	7	7	5	7
-13	7	3	5	-1	1	7	8	40	-51
1	7	4	49	53	-1	7	8	33	-43
-1	7	4	48	54	3	7	8	8	-7
3	7	4	21	31	-3	7	8	4	-8*
-3	7	4	14	13	5	7	8	4	1*
5	7	4	17	15	-5	7	8	4	-7*
7	7	4	28	-28	7	7	8	5	12
9	7	4	19	-21	-7	7	8	8	-15
-9	7	4	5	7	9	7	8	4	16
11	7	4	17	-10	-9	7	8	4	7*
-11	7	4	8	-5	-11	7	8	14	17
-13	7	4	12	-11	1	7	9	16	22
1	7	5	5	-7	-1	7	9	26	27

table 4.5 contd.

3	7	9	16	-26	-12	8	1	5	8*
-3	7	9	16	22	0	8	2	13	-14
5	7	9	21	-22	2	8	2	7	-3
-5	7	9	4	1	-2	8	2	13	15
7	7	9	4	-7*	4	8	2	37	-39
-7	7	9	4	1*	-4	8	2	34	40
9	7	9	8	-13	6	8	2	21	-27
-9	7	9	8	-7	-6	8	2	48	48
1	7	10	15	-16	8	8	2	17	-20
-1	7	10	22	25	-8	8	2	4	1
3	7	10	9	-11	10	8	2	4	-2
-3	7	10	26	32	-10	8	2	12	-15
-5	7	10	4	2*	12	8	2	5	24
7	7	10	4	-5*	-12	8	2	4	-2*
-7	7	10	22	22	0	8	3	20	-22
-9	7	10	4	3	2	8	3	26	-33
1	7	11	23	23	-2	8	3	4	-4*
-1	7	11	11	8	4	8	3	27	-28
3	7	11	12	17	-4	8	3	24	26
-3	7	11	4	-3*	6	8	3	4	-1
5	7	11	4	10*	-6	8	3	31	36
-5	7	11	4	-2*	8	8	3	4	-1*
-7	7	11	4	-4*	-8	8	3	6	9
1	7	12	21	21	10	8	3	4	-4*
-1	7	12	14	26	-10	8	3	11	12
3	7	12	14	19	-12	8	3	4	-5
-3	7	12	4	12*	0	8	4	41	48
-5	7	12	4	8*	2	8	4	33	40
5	7	13	4	10	-2	8	4	31	37
0	8	0	49	-53	4	8	4	29	38
2	8	0	50	-62	-4	8	4	4	12*
4	8	0	27	-37	6	8	4	14	19
6	8	0	31	36	-6	8	4	5	-7
8	8	0	22	22	8	8	4	22	-26
10	8	0	4	0*	-8	8	4	4	-11*
12	8	0	4	2*	10	8	4	31	-35
0	8	1	22	-26	-10	8	4	5	-9
2	8	1	4	-4*	-12	8	4	13	-14
-2	8	1	21	-21	0	8	5	20	18
4	8	1	9	8	2	8	5	18	13
-4	8	1	37	-35	-2	8	5	37	40
6	8	1	36	43	4	8	5	29	-38
-6	8	1	14	-7	-4	8	5	4	3*
8	8	1	19	18	6	8	5	16	-25
-8	8	1	4	3*	8	8	5	4	-11*
10	8	1	5	0	-8	8	5	6	6
-10	8	1	4	-8*	10	8	5	5	-16
12	8	1	9	9	-10	8	5	4	-7*

table 4.5 contd.

0	8	6	4	-3*	3	9	0	8	-12
2	8	6	11	9	5	9	0	4	-18*
-2	8	6	15	-14	7	9	0	4	-14*
4	8	6	20	23	9	9	0	4	-4*
-4	8	6	22	-26	1	9	1	20	-19
6	8	6	28	30	-1	9	1	4	-80
-6	8	6	7	-15	3	9	1	4	-7*
8	8	6	4	15*	-3	9	1	21	-26
-8	8	6	9	-6	5	9	1	11	13
10	8	6	4	-4	-5	9	1	38	-43
-10	8	6	10	-12	7	9	1	21	30
0	8	7	8	5	-7	9	1	4	1*
2	8	7	24	32	9	9	1	14	37
-2	8	7	10	-11	-9	9	1	8	10
4	8	7	15	16	1	9	2	4	-3*
-4	8	7	14	-15	-1	9	2	4	-6*
6	8	7	7	-9	3	9	2	24	34
-6	8	7	4	-4*	-3	9	2	8	-9
8	8	7	4	-2*	5	9	2	22	26
-8	8	7	4	-17*	-5	9	2	8	-11
-10	8	7	4	9*	7	9	2	4	-2*
0	8	8	28	-29	-7	9	2	4	-16*
2	8	8	34	-44	9	9	2	4	10*
-2	8	8	26	-26	-9	9	2	4	-3*
-4	8	8	4	-2*	1	9	3	32	-35
6	8	8	4	2*	-1	9	3	34	-39
-6	8	8	4	6*	3	9	3	15	-21
8	8	8	6	-6	-3	9	3	9	-13
-8	8	8	4	6*	5	9	3	4	0*
0	8	9	25	-37	-5	9	3	4	20*
2	8	9	6	-3	7	9	3	24	-37
-2	8	9	15	-22	-7	9	3	4	6*
4	8	9	6	15	9	9	3	15	19
-4	8	9	13	-22	-9	9	3	25	30
6	8	9	13	18	1	9	4	9	-7
-6	8	9	4	-13*	-1	9	4	9	8
-8	8	9	4	2*	3	9	4	4	4*
0	8	10	4	-0*	-3	9	4	4	-2*
2	8	10	4	-2*	5	9	4	19	26
-2	8	10	4	9*	-5	9	4	4	2*
4	8	10	4	-6*	7	9	4	4	14*
-4	8	10	16	23	-7	9	4	4	9
-6	8	10	17	20	9	9	4	4	1*
0	8	11	4	-7	-9	9	4	8	7
2	8	11	16	-19	1	9	5	4	7*
-2	8	11	6	6	-1	9	5	27	27
-4	8	11	4	9	3	9	5	4	5*
1	9	0	4	-3*	-3	9	5	25	41

table 4.5 contd.

5	9	5	8	7	0	10	2	4	3*
-5	9	5	12	12	2	10	2	21	23
7	9	5	27	-38	-2	10	2	11	-17
-7	9	5	4	12*	4	10	2	10	20
-9	9	5	4	-5*	-4	10	2	12	17
1	9	6	4	3	6	10	2	4	6
-1	9	6	4	7	-6	10	2	24	-28
-3	9	6	5	-8	0	10	3	8	-9
-3	9	6	7	11	2	10	3	9	11
5	9	6	12	-26	-2	10	3	4	-8
-5	9	6	17	22	4	10	3	4	0*
7	9	6	4	-4*	-4	10	3	4	-11
-7	9	6	4	9*	6	10	3	4	1*
1	9	7	35	45	-6	10	3	15	16
-1	9	7	23	27	0	10	4	4	-3*
3	9	7	16	27	2	10	4	7	-10
-3	9	7	4	-17*	-2	10	4	9	-14
5	9	7	16	32	4	10	4	4	-13*
-5	9	7	4	-7*	-4	10	4	4	-1*
-7	9	7	4	-5*	6	10	4	4	5*
1	9	8	4	2*	-6	10	4	4	5*
-1	9	8	4	1*	0	10	5	4	-16*
3	9	8	4	0*	2	10	5	9	15
-3	9	8	4	5*	-2	10	5	4	2*
5	9	8	4	-21	4	10	5	4	7*
-5	9	8	4	5*	-4	10	5	4	1*
1	9	9	9	-7	-6	10	5	4	-3*
-1	9	9	4	-3*	0	10	6	4	-11*
3	9	9	7	7	2	10	6	4	-10*
-3	9	9	14	-22	-2	10	6	4	6*
-5	9	9	4	-6	4	10	6	16	-21
0	10	0	28	32	-4	10	6	4	21*
2	10	0	22	24	0	10	7	4	13*
4	10	0	4	-5	2	10	7	10	15
6	10	0	4	-9	-2	10	7	4	3*
0	10	1	4	-1*	1	11	0	4	11*
2	10	1	4	-4*	1	11	1	7	17
-2	10	1	7	7	-1	11	1	4	2*
4	10	1	20	-21	1	11	2	4	5*
-4	10	1	4	-6*	-1	11	2	7	10
6	10	1	5	-10	3	11	3	4	4*
-6	10	1	4	1*					

APPENDIX I

A Computer Program to Calculate φ , χ and 2Θ Settings of the Goniostat

I.1 Program Description

This program has been written in in Fortran IV language for IBM 704 computer. This is a general program for monoclinic or higher symmetry crystals. It accepts a, b, c, and β as input data and produces a set of h, k, l, φ , χ and 2Θ properly sorted in desired order. The main features of the program are discussed in the following sections.

I.2 2Θ Shell Selection

The whole sphere of reflection can be divided into a number of shells of 2Θ . The width of each shell in degrees and the number of shells is selected through a data card.

I.3 Selection of Quadrant

The program expects a quadrant selection control card to decide which of the four i.e. hkl, $\bar{h}kl$, $h\bar{k}l$ and $h k \bar{l}$ has to be calculated. The quadrant selection is done through a subroutine QDRNT.

I.4 Systematic Absences

If desired the program can be instructed not to calculate the systematically absent reflections. This suppression of calculation is done through a subroutine SYSTAB. This subroutine is different for different space groups.

I.5 Calculation

The lattice parameters a, b, c, α, β , and γ are used to calculate the reciprocal lattice parameters a^*, b^*, c^* and β^* . The angles $2\theta, \varphi$ and χ are calculated according to the following relations

$$2\theta_{hkl} = 2\sin^{-1}\left(\frac{\lambda}{2\sqrt{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hla^*c^* \cos\beta^*}}\right) \quad \dots(I-1)$$

$$\varphi_{hkl} = \cos^{-1}\left(\frac{l^2 c^{*2} + 2hla^*c^* \cos\beta^*}{2ha^*\sqrt{h^2 a^{*2} + l^2 c^{*2} + 2a^*c^*h1 \cos\beta^*}}\right) \quad \dots(I-2)$$

$$\chi_{hkl} = \tan^{-1}\left(\frac{kb^*}{\sqrt{h^2 a^{*2} + l^2 c^{*2} + 2hla^*c^* \cos\beta^*}}\right) \quad \dots(I-3)$$

I.5 Sorting

When all the reflections of a quadrant in a 2θ shell are calculated, they are sorted on φ, χ and 2θ in the order desired through a subroutine FSRT.

Finally the output is printed in a tabular fashion leaving spaces for writing down the peak counts and the background counts for each reflection.

APPENDIX II

Data Reduction Program

II.1 Program Description

This program is written in Fortran IV language for IBM 7044 computer. This program accepts h, k, l , the peak count and the background counts as input and applies correction to the intensities and prepares properly sorted input data for the structure factor or the least square refinement program.

II.2 Corrections

The program calculates mean background from the background counts of high and low 2Θ side. This background is subtracted from the peak counts and appropriate Lorentz and Polarization corrections are applied to the intensities. These corrected intensities I_{hkl} are then converted to $|F_{hkl}|$ through the following relation.

$$K |F_{hkl}| = \sqrt{I_{hkl}} \quad \dots(II-1)$$

II.3 Sorting and Output

All the reflections are then sorted on the Miller indices h, k, l in the order specified and a data file is created on a magnetic tape. This file can be used as input data for the structure factor program or the least square refinement program.

GENERAL REFERENCES

1. H. Lipson and W. Cochran "The Determination of Crystal Structures", G. Bell and Sons Ltd. (1966).
2. R.W. James "The Optical Principles of the Diffraction of X-Rays", G. Bell and Sons Ltd. (1967).
3. M.J. Buerger "Crystal Structure Analysis", John Wiley and Sons Inc. (1967).
4. "International Table For X-Ray Crystallography Vol. I", Kynoch Press, Birmingham (1965).
5. "International Table For X-Ray Crystallography Vol. III", Kynoch Press, Birmingham (1965).

REFERENCES

1. R.H. Balundi and A. Chakravorty, Inorg. Nucl. Chem. Letters, 2, 167 (1973).
2. W.R. Busing and H.A. Levy, Acta Cryst. 10, 180 (1957).
3. R.C. Srivastava and E.C. Lingafelter, Acta Cryst. 20, 918 (1966).
4. M.J. Buerger "Crystal Structure Analysis", John Wiley and Sons Inc. (1967).
5. A.L. Patterson, Z. Krist. A90, 517 (1935).
6. G.A. Sim, Acta Cryst. 10, 177 (1957).
7. A.D. Booth, Phil. Mag., 36, 609 (1945).
8. A.D. Booth, Nature 161, 765 (1948).
9. W. Cochran, Acta Cryst., 4, 81 (1951).
10. W. Cochran, Acta Cryst., 4, 408 (1951).
11. E.W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941).
12. Y.C. Leung, R.E. Marsh and V. Schoemaker, Acta Cryst., 10, 650 (1957).
13. D.W.J. Cruickshank "Computing Methods in Crystallography", Pergman Press Oxford (1965).
14. Appendix I
15. M.V. Stakleberg, Z. Inorg. Chem., 253, 136 (1947).
16. Appendix II
17. A.J.C. Wilson, Nature 150, 152 (1942).
18. W.R. Busing, K.O. Martin and H.A. Levy, Program Report ORNL-TM-305, Oak Ridge National Laboratories (1962).
19. International Tables For X-Ray Crystallography Vol. III, Birmingham, Kynoch Press (1962).
20. F. Mazzi, R.C. Soc. Mineral, Ital., 2, 148 (1953).

21. Y. Komiyama and E.C. Lingafelter, *Acta Cryst.*, 17, 1145 (1964).
22. A. Sugihara, T. Ashida, Y. Sasada, M. Kakudo, *Acta Cryst.*, B24, 203 (1968).
23. B.W. Brown and E.C. Lingafelter, *Acta Cryst.*, 17, 254 (1964).
24. D.S. Brown, J.D. Lee and B.G.A. Melsom, *Acta Cryst.*, B24, 730 (1968).
25. H. Scoulondi, *Acta Cryst.*, 6, 651 (1953).
26. S.J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 89, 3331 (1967).
27. G. Arai, J. Coppola and G.A. Jeffrey, *Acta Cryst.*, 13, 553 (1960).
28. T.A. Hamor, W.S. Caughery and J.L. Hoard, *J. Chem. Phys.*, 43, 3100 (1965).
29. T.L. Hoard, M.J. Hamor, T.A. Hamor and W.S. Caughey, *J. Amer. Chem. Soc.*, 87, 2312 (1965).
30. R.H. Balundi and A. Chakravorty, *Inorg. Chem.* (In press).
31. H. Lipson and W. Cochran "The Determination of Crystal Structures", G. Bell and Sons Ltd. (1966).
32. W.R. Busing, K.O. Martin and H.A. Levy, Program Report ORNL-TM-305 Oak Ridge National Laboratory (1962).
33. G. Marngiu, E.C. Lingafelter and P. Paoletti, *Inorg. Chem.*, 8, 2763 (1969).
34. B.W. Brown and E.C. Lingafelter, *Acta Cryst.*, 17, 254 (1964).
35. Y. Komiyama and E.C. Lingafelter, *Acta Cryst.*, 17, 1145 (1964).
36. A work done at University of Washington reffered to in *Inorg. Chem.*, 8, 2763 (1969).

